NATURE OF THE RADICAL INTERMEDIATES IN A SUBSTITUTED CYCLOPROPYLCARBINYL--ALLYLCARBINYL SYSTEM

Thesis by

Thomas A. Halgren

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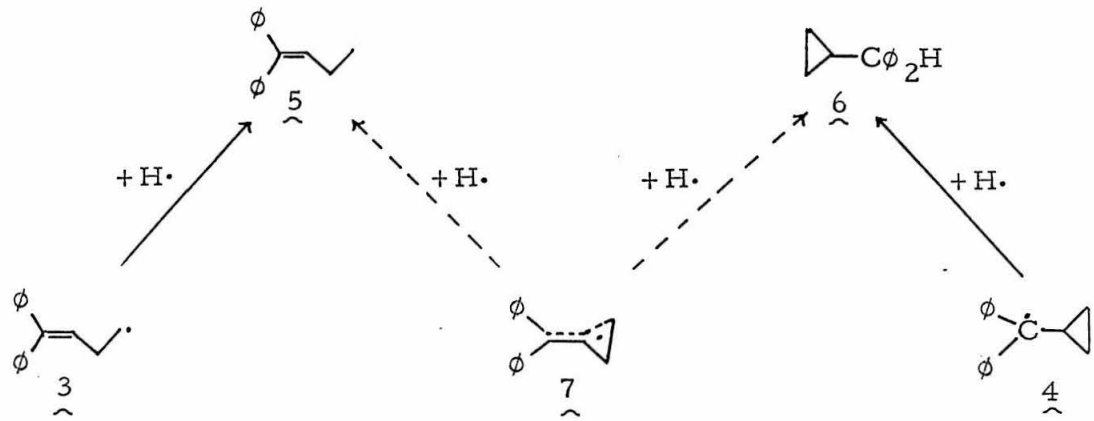
ABSTRACT

We have sought to determine the nature of the free-radical precursors to ring-opened hydrocarbon 5 and ring-closed hydrocarbon 6. Reasonable alternative formulations involve the postulation of hydrogen abstraction (a) by a pair of rapidly equilibrating classical radicals (the ring-opened allylcarbinyl-type radical 3 and the ring-closed cyclopropylcarbinyl-type 4), or (b) by a nonclassical radical such as homoallylic radical 7.

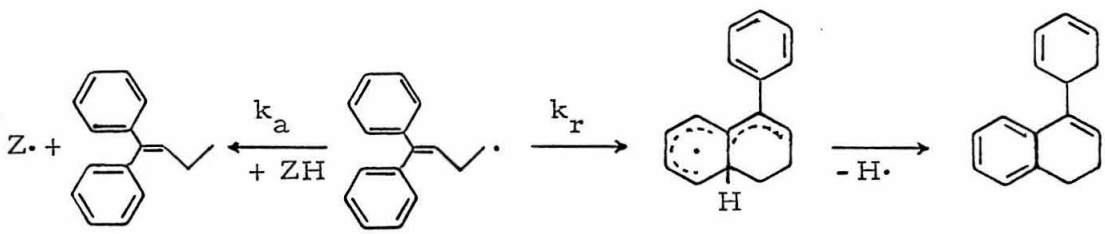


Entry to the radical system is gained via degassed thermal decomposition of peresters having the ring-opened and the ring-closed structures. The ratio of 6:5 is essentially independent of the hydrogen donor concentration for decomposition of the former at 125° in the presence of triethyltin hydride. A deuterium labeling study showed that the α and β methylene groups in 3 (or the equivalent) are rapidly interchanged under these conditions.

Existence of two (or more) product-forming intermediates is indicated (a) by dependence of the ratio 6:5 on the tin hydride concen-

tration for decomposition of the ring-closed perester at 10 and 35°, and (b) by formation of cage products having largely or wholly the structure (ring-opened or ring-closed) of the starting perester.

Relative rates of hydrogen abstraction by 3 could be inferred by comparison of ratios of rate constants for hydrogen abstraction and ortho-ring cyclization:



5 3 9 10

At 100° values of k_a/k_r are 0.14 for hydrogen abstraction from 1,4-cyclohexadiene and 7 for abstraction from triethyltin hydride. The ratio 6:5 at the same temperature is ~0.0035 for hydrogen abstraction from 1,4-cyclohexadiene, ~0.078 for abstraction from the tin hydride, and ≥5 for abstraction from cyclohexadienyl radicals. These data indicate that abstraction of hydrogen from triethyltin hydride is more rapid than from 1,4-cyclohexadiene by a factor of ~1000 for 4, but only ~50 for 3.

Measurements of product ratios at several temperatures allowed the construction of an approximate energy-level scheme. A major inference is that isomerization of 3 to 4 is exothermic by 8 ± 3 kcal/mole, in good agreement with expectations based on bond dissociation energies. Absolute rate-constant estimates are also given.

The results are nicely compatible with a classical-radical

mechanism, but attempted interpretation in terms of a nonclassical radical precursor of product ratios formed even from equilibrated radical intermediates leads, it is argued, to serious difficulties.

The roles played by hydrogen abstraction from 1,4-cyclohexadiene and from the derived cyclohexadienyl radicals were probed by fitting observed ratios of $\underset{\sim}{6}:\underset{\sim}{5}$ and $\underset{\sim}{5}:\underset{\sim}{10}$ in the sense of least-squares to expressions derived for a complex mechanistic scheme. Some 30 to 40 measurements on each product ratio, obtained under a variety of experimental conditions, could be fit with an average deviation of $\sim 6\%$. Significant systematic deviations were found, but these could largely be redressed by assuming (a) that the rate constant for reaction of $\underset{\sim}{4}$ with cyclohexadienyl radical is inversely proportional to the viscosity of the medium (i.e., is diffusion-controlled), and (b) that k_a/k_r for hydrogen abstraction from 1,4-cyclohexadiene depends slightly on the composition of the medium. An average deviation of 4.4% was thereby attained.

Degassed thermal decomposition of the ring-opened perester in the presence of the triethyltin hydride occurs primarily by attack on perester of triethyltin radicals, presumably at the -O-O- bond, even at 0.01 M tin hydride at 110 and 125°. Tin ester and tin ether are apparently formed in closely similar amounts under these conditions, but the tin ester predominates at room temperature in the companion air-induced decomposition, indicating that attack on perester to give the tin ether requires an activation energy approximately 5 kcal/mole in excess of that for the formation of tin ester.

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AN OVERVIEW

Theses, at least those recently submitted in Chemistry at this Institution, generally begin with an introduction in which the stage is set for the presentation of the current results and conclusions. That, however, is not the principal purpose of this section. To be sure, a liberal amount of stage-setting will be indulged, but generally at appropriate points later in the text.

As this thesis describes work in the field of free-radical rearrangements in small-ring compounds, an argument can be made for including a comprehensive introduction for the convenience of readers not reasonably conversant with the field. However, treatments of suitable length and scope are available in reasonably accessible sources, and this thesis is quite long enough as it is. I shall therefore simply list here available treatments and leave it to the reader to make whatever use of them he wishes.

The introductory section to a recent paper by Montgomery (1) conveys rather briefly (two and a half journal pages) the essential flavor of the field. Though structured to suit his particular uses, the discussion is appropriate here as well, for both Montgomery's work and mine emphasize rearrangements between cyclopropylcarbinyl radicals and their allylcarbinyl counterparts. The first and third subsections (about 25 pages) of the introduction to Rosen's 1964 thesis (2) discuss skeletal rearrangements of this particular type. The introduction (30 pages) to Schuster's 1961 thesis (3) covers much of the same

ground, but includes as well a discussion of radical rearrangements in a number of other systems. Pryor's recent book "Free Radicals" (4) contains an easily readable chapter covering the literature on radical rearrangements through 1964. Finally, comprehensive literature reviews have been supplied by Walling (5) and by Freidlina (6).

1. Purpose of this Overview

The subject of this thesis is a complex one. In the spirit of the greatest possible clarity, no attempt will be made to use the detective-story mode of presentation. Indeed, the opposite will be attempted; to show the pattern of the results and their interpretation as early as possible and, in steadily increasing depth of rigor and sophistication, to demonstrate the validity of the interpretation. To this end, this section is intended to give a brief overview of the principal results obtained in this work and of the approach we shall take in seeking to interpret those results.

2. A Few Comments on Terminology

Some 28 compounds or intermediates not possessing conveniently short trivial names are discussed on multiple occasions in this thesis. Because it would be awkward to give, at each mention, the full chemical name, the various compounds have been assigned numbers in the order of their appearance in the text. I have been importuned to realize, however, that a total reliance on numerical designations places a severe strain on the reader unless a structure is indicated

after any sizable gaps between the occasions that the associated number is used. A mixed system has therefore been employed. A numbered compound will be referenced by its number if the relationship between the number and the structure has been recently reinforced; or by a valid chemical name; or by use of an established synonym, generally in conjunction with the numerical designation. Synonyms may be contractions on the chemical name (e. g., diphenylbutene or the butene for 1, 1-diphenyl-1-butene), but more commonly characterize some structural feature of the referenced compound (e. g., 'ring-opened hydrocarbon' and 'ring-closed hydrocarbon' for 1, 1-diphenyl-1-butene and diphenylcyclopropylmethane, respectively).

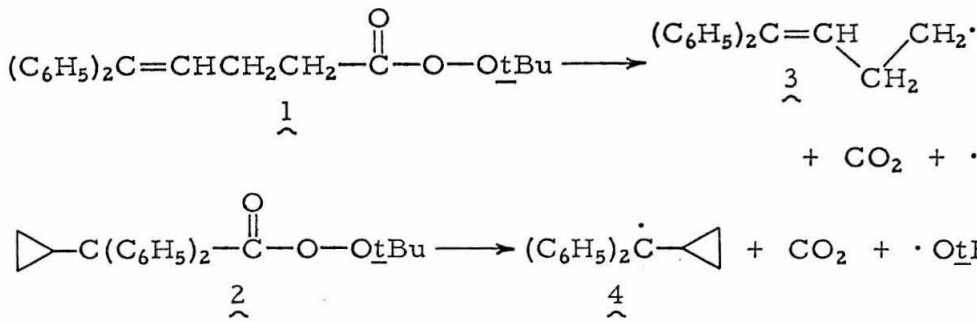
The reader may find quite useful the listing of numbers and structures enclosed in a jacket on the inside back cover. A second copy has been placed preceding the list of references for use in microfilmed copies of this thesis.

3. A Brief Overview of Principal Results and Conclusions

Nonacid-catalyzed thermal decomposition of t-butyl peresters appears to be a general means of generating alkyl or aryl free radicals of reasonably predetermined structure (7). For example, if one wished to study ethyl radicals, the perester of choice would be t-butyl perpropanoate, $CH_3CH_2CO_2OtBu$. Similarly, a radical R· could be prepared by thermolysis of the structurally related perester, as below:

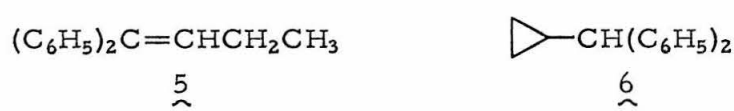
$$R-\overset{\overset{O}{\|}}{C}-O-OtBu \longrightarrow R\cdot + CO_2 + \cdot OtBu$$

Thermal decomposition of the isomeric peresters 1 and 2 would then be expected to generate the radicals 3 and 4, respectively. The



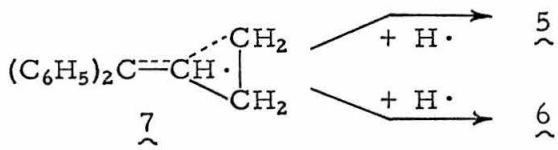
principal goal of this research has been to characterize the chemical behavior of the 16-carbon radicals generated in this way. Perhaps the most interesting aspect of this problem arises from the possibility that radicals with ring-opened and ring-closed structures can interconvert. For example, attack of the radical center in ring-opened radical 3 on the nearer of the olefinic carbons produces the isomeric radical 4. Similarly, 3 can be regenerated from 4 by the opening of one of the two equivalent cyclopropyl-ring bonds.

This suggests that products with both ring-opened and ring-closed structures might be formed whichever the perester employed. Such is indeed the case. In particular, the ring-opened hydrocarbon 1,1-diphenyl-1-butene (5) and the ring-closed diphenylcyclopropylmethane (6) are produced via abstraction of hydrogen from suitable hydrogen donors.



The radical precursors of 5 and 6 might well be the ring-opened and ring-closed radicals 3 and 4, each giving the structurally related

hydrocarbon. However, the situation need not be so simple, for it is conceivable that a bridged "nonclassical" radical such as 7 (which represents a structural compromise between the limiting forms 3 and 4) might give rise upon hydrogen abstraction either to ring-opened or to ring-closed material. (A general definition of what might be meant by



a nonclassical radical will be attempted in Section Three. For the present I shall assume familiarity with the concept as embodying attack of a reagent at more than one site and as possibly associated with unusually rapid rates of formation of intermediates.)

Thus, a principal purpose of the present account will be to marshal evidence on the nature of the radical intermediates which give rise to the isomeric hydrocarbons 5 and 6. As will become apparent, however, this thesis really has two stories to tell. The second will be to give a mechanistic description of the rather complicated sequence of reactions by which radicals generated as above are converted to the several stable products under a variety of experimental conditions.

In reality, the two stories are intimately related. Some of the observations and interpretations we shall find to be of great importance in deciding on the involvement of a species such as 7 do not leap unencumbered from the experimental data, but rather arise from a detailed characterization of the reaction mechanism. Moreover, for other cases in which interpretation of the data is apparently straight-

forward, our confidence in those interpretations will be greatly enhanced by the general success of the mechanistic formulation.

In a spirit of reciprocity, it might be asked whether the mechanistic study does not itself require assumptions concerning the nature of the intermediates which give rise to the isomeric hydrocarbons 5 and 6; and if so, whether such assumptions do not prejudice the interpretation of the data. In general, the answer is that such assumptions will frequently be made, but that the interpretation of the data is not prejudiced. The reason is that the intermediates giving rise to 5 and 6, whatever their nature, are generally in rapid equilibrium; and as every good kineticist knows, under such circumstances the form of derived equations is independent of which reactions are attributed to which of the equilibrated species. Alternative assignments change the interpretation of various parameters, but the matter of interpretation can be taken up after the values of the parameters have been extracted from the data.

In the remaining pages of this Overview we shall make a start on each of the two stories. First we shall indicate why we have chosen to examine the present system for the intervention of a nonclassical radical such as 7 and we will give some examples of the types of information employed in that examination. Then we will survey the main features of the overall reaction mechanism and indicate the approach to be taken in giving a more complete description later in the thesis.

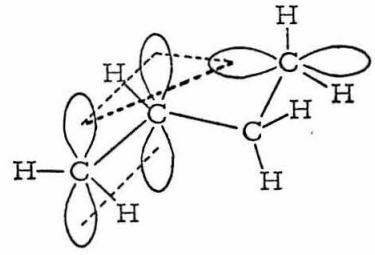
The nonclassical carbonium ion problem has commanded substantial interest over the past two decades. The reprint collection

"Nonclassical Ions" edited by Bartlett features many important papers in this field (8). As is well known, kinetic evidence points to very large driving forces in some systems for the bridging-with-charge-delocalization associated with the formation of the nonclassical ion. In contrast, there seem to be no analogous examples of nonclassical hydrocarbon free radicals (we exclude here bromine-bridged radicals (9)), even though the free-radical chemistry of several of the systems showing exotic behavior in carbonium ion reactions has been investigated. For example, formation of norbornyl or 5-norbornenyl radicals is unexceptional on kinetic grounds (10, 11). Moreover, the results of products studies on the 5-norbornenyl-nortricyclyl radical system are inconsistent with the sole intermediacy of a nonclassical radical capable of giving products of either structural form (12).

Apparently, in many cases the driving force for formation of a bridged intermediate in a carbonium ion system is wholly or entirely lost upon addition of the extra electron possessed by the analogously constituted free-radical system. It may be significant that semi-empirical molecular orbital calculations predict that this might be the case (13). Still, it is not yet clear that the diminished driving force will preclude altogether the formation of nonclassical radical intermediates. In attempting to resolve this uncertainty, it seems reasonable to carefully examine the free-radical chemistry of additional systems which apparently show substantial inclination toward formation of nonclassical intermediates in carbonium ion reactions; the present work is a case in point.

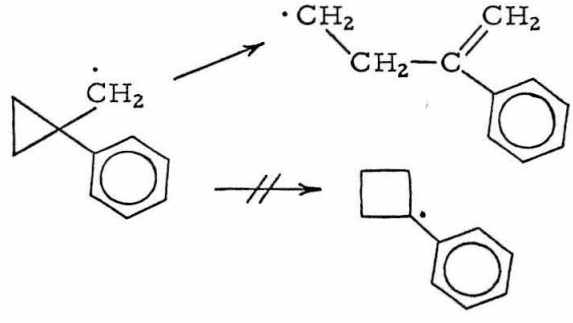
The facile interconversions of isomeric allylcarbinyl, cyclopropyl-

carbinyl, cyclobutyl systems in carbonium ion systems is well known and has been plausibly interpreted in terms of nonclassical bicyclobutonium ions (14). The sketch below indicates a proposed structure



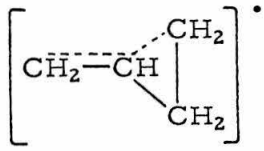
for the parent four-carbon bicyclobutonium ion (13a). Attack of solvent or an anion on the carbon at lower left leads to cyclopropylcarbinyl product. Similarly, attack at upper right gives allylcarbinyl product, and attack at the central carbon leads to cyclobutyl product.

One principal difference in the chemistry of analogously constituted radical intermediates is that allylcarbinyl and cyclopropylcarbinyl structures do not seem to be interconvertible with cyclobutyl structures (15). This generalization holds even where substitution should strongly promote just such an interconversion (15a):



For this reason, speculation on nonclassical free-radical intermediates in this type of system has focused on structures of the so-called homo-

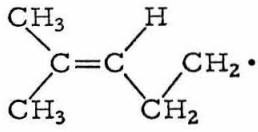
allylic type, as below:

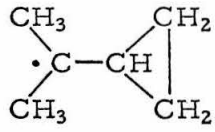


Free-radical studies on the parent 4-carbon system have been reported by several groups. Kinetic evidence indicates that the cyclopropylcarbinyl radical is formed substantially more easily than a typical primary radical (16). However, products studies have proved disappointing in that on hydrogen abstraction at best trace amounts of cyclopropylmethane are formed (17). Only in the chlorination of cyclopropylmethane have substantial amounts of the cyclopropylcarbinyl product been observed (16b, 18). These results have been reviewed by Rosen (2).

Evidently, if classical cyclopropylcarbinyl and allylcarbinyl radicals are involved, the former is less stable than the latter. Alternatively, if products are formed via a nonclassical species, that species probably closely resembles the allylcarbinyl radical. In either case, it seemed reasonable to try to effect closer competition by selectively stabilizing the cyclopropylcarbinyl form.

The ring-opened and ring-closed radicals for the dimethyl-substituted system are shown below. However, product studies here have





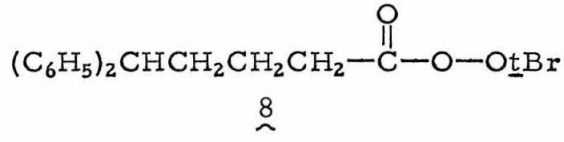
also been generally disappointing. Thus, radical-chain reduction

of γ,γ-dimethylallylcarbinyl bromide by tri-n-butyltin hydride gave dimethylbutene with only a trace (less than 0.2%) of isopropylcyclopropane (19a). In contrast, decarbonylation of dimethylcyclopropylacetaldehyde did give 18% isopropylcyclopropane when carried out in the presence of approximately 3 M benzylmercaptan (19b). However, the reaction appears to be too complex to permit dilineation of the mechanistic pathways by which this material was formed (20).

Phenyl groups would be expected to be much more effective than methyl groups in increasing the stability of the ring-closed radicals. Accordingly, Howden (21) ran a preliminary investigation on the diphenyl-substituted system using perester 1 as a radical source. The most encouraging results were obtained when tri-n-butyltin hydride was employed as the hydrogen donor (see Table 12, p. 44). In particular, ring-opened hydrocarbon 5 and ring-closed hydrocarbon 6 are observed in proportions of about twenty to one for decomposition of 1 from 110 to 150° and 0.056 to 0.56 M in the initial tin hydride concentration. The lack of any substantial product dependence on the hydrogen donor concentration is consistent either with a mechanism in which both products are formed from a nonclassical radical such as 7, or with one in which the two classical radicals (3 and 4) are able to equilibrate rapidly with respect to hydrogen abstraction by either. Mechanisms involving both classical and nonclassical radicals are also possible, but for simplicity it seems desirable to restrict our attention, at least initially, to the two limiting possibilities.

Unlike the unsubstituted system discussed previously, the available kinetic evidence does not suggest that radical intermediates are

formed more easily than might be expected from model compounds. Howden measured the rates of decomposition in chlorobenzene at 110° of ring-opened perester 1 and its saturated analogue 8. He found that the former decomposes only about 40% faster than the latter. Further-



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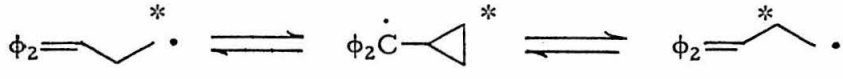
more, the rate constant for 1 is nearly the same as the rate constants observed by Trachtman and Miller for a series of peresters in which the R group is long-chain primary aliphatic (22). Half-lives for 1 and 8 and for two of the four cases studied by Trachtman and Miller are listed in Table 13, p. 51.

A detailed discussion of structure and reactivity of peresters is deferred until Section One. However, we can point out here that peresters giving phenyl-stabilized radicals decompose three and four orders of magnitude faster than primary aliphatic peresters (see Table 13). Thus, direct formation of a nonclassical radical from 1 should be accompanied by a large rate increase, unless the decrease in the energy of activation expected to be associated with any bridging in the decomposition transition state should happen to be largely balanced by the decrease in entropy associated with the greater restriction bridging implies. Activation parameters would be useful in this connection, but are unavailable.

We shall accept, with Howden (23), the implication that the classical ring-opened radical 3 is formed upon decomposition of per-

ester 1. However, 3 might rapidly isomerize to 7, with that species then giving rise to the hydrocarbon products. To rule on that eventuality, we shall have to turn to studies on product composition.

One way in which the existence of a nonclassical radical such as 7 might be demonstrated is suggested by the elementary discussion of the interconversion of the classical radicals given on page 4. Because regeneration of the ring-opened radical 3 from 4 can be effected by the opening of either of two cyclopropyl-ring bonds, equilibration of the



3 4 3

classical radicals must exchange the methylene groups of the ring-opened radical; and the presence or absence of such an exchange can be detected by suitable labeling. Using deuterium labeling it has been found (p. 94-97) that the methylene-group exchange is rapid with respect to hydrogen abstraction from triethyltin hydride (1.3 M) at 125°.

We should note, however, that while the absence of exchange would point to the intermediacy of a nonclassical radical, the finding that the exchange proceeds does not suffice to disprove the intermediacy of such a species. If a nonclassical radical were only slightly more stable than the classical ring-closed radical, equilibrium between the two might be rapidly established, and this process would exchange the methylene groups.

In seeking to establish the nature of the radical intermediates, information on their number would be especially valuable. Such information can now be reported. Specifically, the ratio of ring-closed

to ring-opened hydrocarbon for decomposition of the (more reactive) ring-closed perester 2 at 10 and 35° in the presence of triethyltin hydride is not independent of the tin hydride concentration, but increases in a linear fashion (Fig. 8, p. 100) as is predicted for selective trapping of a first-formed radical intermediate. That species might well be the classical ring-closed radical 4, but the actual observations do not demand this interpretation. What is established is that more than one radical intermediate gives rise to the isomeric hydrocarbons.

Information is also available concerning the dependence of the ratio of the two hydrocarbons on the reactivity of the hydrogen donor and on the reaction temperature.

The response of the radical system to the nature of the hydrogen donor has been probed using three hydrogen donors which cover a wide range in reactivity. The three are: 1,4-cyclohexadiene, possibly one of the most active of purely hydrocarbon donors; triethyltin hydride, indicated by several measures to be substantially more active than 1,4-cyclohexadiene; and the cyclohexadienyl radical, expected to be extremely reactive because it acts as a hydrogen donor in disproportionation-type reactions which are known to have high preexponential factors and minimal or nonexistent activation energies. The quantity of interest here is the ratio of ring-closed hydrocarbon 6 to ring-opened hydrocarbon 5 under conditions in which the radicals involved have sufficient time to reach equilibrium amongst themselves; we will call this quantity (which may not always be directly measurable) the characteristic ratio. Characteristic ratios at 100° are 0.0035 for 1,4-cyclohexadiene, 0.08 for triethyltin hydride, and greater (pos-

sibly by orders of magnitude) than 5 for the cyclohexadienyl radical.

Characteristic ratios will be temperature dependent unless the transition states for hydrogen abstraction leading to the two hydrocarbons (see Fig. 23, p. 333) happen to be of identical energy. If the transition state for formation of the ring-closed hydrocarbon lies below that for formation of the ring-opened isomer, the relative amount of the ring-closed isomer will be greater at lower reaction temperatures. This is the pattern observed experimentally for the hydrogen donors 1,4-cyclohexadiene and triethyltin hydride. Transition-state energy differences are found to be 1-2 kcal/mole for the former and 3 kcal/mole for the latter. In addition, a good argument can be made that the cyclohexadienyl radical conforms to the pattern with a difference of about 8 kcal/mole.

We shall find that such observations are easily explained if one assumes that only classical radicals are involved, but that a nonclassical radical would have to behave very strangely indeed to reproduce the experimental observations.

Additional information which cannot be so directly stated is brought out in Sections One and Two of this thesis in the course of the detailed mechanistic treatment.

The reader may be curious to know how information on the characteristic ratio for hydrogen abstraction from cyclohexadienyl radicals was obtained. In general, one simply employs a hydrogen donor of interest as solvent. Such a course would clearly be impossible for a free-radical donor. It is possible, however, to generate

cyclohexadienyl radicals in situ by allowing the peresters to decompose in the presence of 1,4-cyclohexadiene, whence some of the radicals abstract hydrogen from cyclohexadiene.

Because 1,4-cyclohexadiene and the derived cyclohexadienyl radicals can both serve as hydrogen donors, a mechanistic analysis is required to determine which products of interest result from hydrogen abstraction from which of these donors, and, indeed, to evaluate whether the observations can successfully be accounted for on any such basis. The mechanistic study of Section Two will focus primarily on results obtained for decomposition of the peresters (at various initial concentrations) in the presence of 1,4-cyclohexadiene (also at various initial concentrations) and at various reaction temperatures. However, it will also be instructive and reassuring to correlate in a similar manner the less extensive data for decomposition of the peresters in the presence of triethyltin hydride.

It will be helpful to subdivide the task of establishing a reaction mechanism. In the first part (Section One) we shall construct a mechanistic scheme to account for the dozen or so reaction products. In the second (Section Two) we shall derive and test mechanistic expressions based on that scheme.

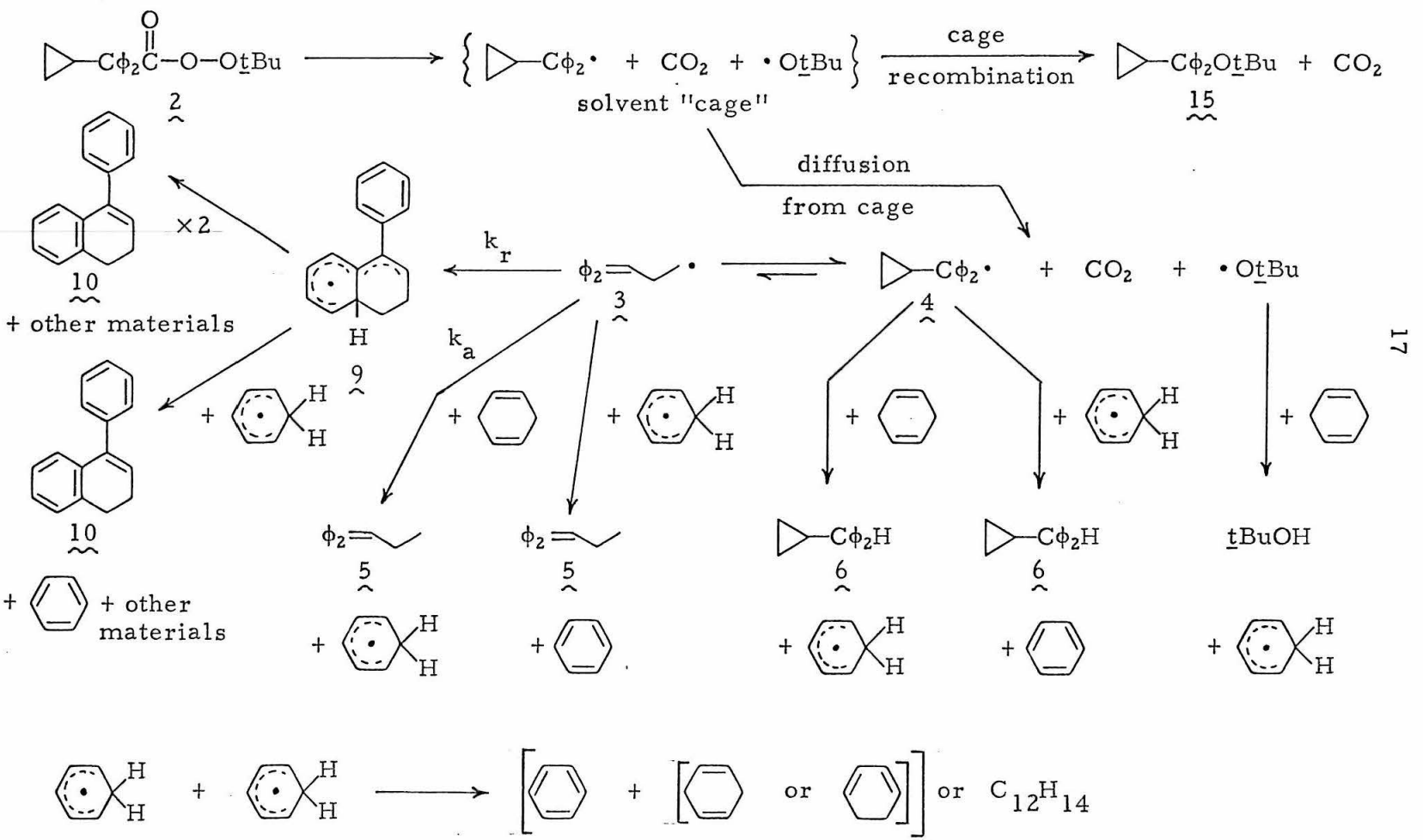
To impart a workable measure of order to the construction of the trial mechanistic scheme, we shall follow in time the fate of a pair of free-radical intermediates produced simultaneously by decomposition of a perester molecule. This procedure is suggested by our observations which indicate that the major reaction steps fall into a

number of classes associated with reasonably well-separated characteristic times. Time limits for some of the processes are given below. Because certain of the processes have appreciable activation energies the time limits will, of course, vary widely with the reaction temperature. The numbers cited below refer to a reaction temperature of 100°.

The reactions discussed here are depicted in Chart 1. For simplicity (vide infra), we shall consider the decomposition of the ring-closed perester 2 rather than that of the ring-opened perester 1. We start our clock at the moment a perester molecule fragments. The products of that fragmentation may be taken to be a ring-closed radical 4, a molecule of carbon dioxide, and a t-butoxy radical. Because the radical pair is initially separated by only a few angstroms, (re)-combination or disproportionation of the radical pair competes with diffusive separation. Such reactions, said to occur within an initial solvent cage (which is indicated by curly brackets in Chart 1), are probably important to times up to about 10^{-9} seconds; if reaction is not effected within this period, diffusion may be expected to have increased the separation of the radical pair to such an extent that subsequent reaction between the once-caged radicals will be improbable (24). Cage recombination to form the t-butyl ether 15 is illustrated in Chart 1; disproportionation to t-butyl alcohol and diphenylmethylenecyclopropane (16) apparently occurs as well.

We shall find that equilibration of the ring-opened and ring-closed radicals is inappreciable during the time in which nearly all of the cage product is formed, but appears to be nearly complete by 10^{-8} seconds after the fragmentation. The nature of the kinetics is

Chart 1. A Partial Mechanistic Scheme for Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate in the Presence of 1,4-Cyclohexadiene.



such that this figure would apply for decomposition at 100° of either perester. Only for triethyltin hydride can hydrogen abstraction compete with the establishment of the equilibrium. Even in this case, effective competition requires temperatures much lower than 100°; as remarked earlier, selective trapping of the first-formed intermediate is observed at 10 and 35°. Evidently, the processes which interconvert the radical intermediates slow more strongly as the reaction temperature is decreased than do the hydrogen abstraction processes when the hydrogen donor is triethyltin hydride.

Formation of the ring-opened and ring-closed hydrocarbons can proceed until about 10^{-4} sec after the fragmentation. The time limit of this case is established by the rate of ortho-ring-cyclization by (presumably) the ring-opened radical 3 to the so-called ring-cyclized radical 9 (see Chart 1). This process is an intramolecular analog of the addition of free radicals to aromatic systems which has been extensively investigated by Szwarc and co-workers (25).

Rate constants for the two processes are denoted by k_r for the ring-cyclization and k_a for hydrogen abstraction by the ring-opened radical from hydrogen donor ZH. The major product from the ring-cyclized radicals is 1-phenyl-3,4-dihydronaphthalene (10), formed principally by disproportionation of ring-cyclized radicals or by loss of a hydrogen atom to solvent radical Z· by 9. As conversion of 9 to 10 is fairly efficient, we can write approximately

$$\frac{d(5)}{d(10)} \cong \frac{k_a(ZH)(3)}{k_r(3)} ,$$

so that

$$\frac{k_a}{k_r} \simeq \frac{\text{Yield of } \underset{\sim}{5}}{\text{Yield of } \underset{\sim}{10} \times (ZH)_{av}}$$

Values of k_a/k_r estimated for the hydrogen donors triethyltin hydride, 1,4-cyclohexadiene, and indene (taking approximately into account the inefficiency in the conversion of $\underset{\sim}{9}$ to $\underset{\sim}{10}$) are about 7, 014, and 0.03, respectively at 100°. All other solvents investigated (cyclohexane, ether, tetrahydrofuran, benzene, cumene, tetraethyltin) are so much less active as hydrogen donors that only trace amounts of the diphenylbutene $\underset{\sim}{5}$ are formed. By this test, then, triethyltin hydride is clearly more active a hydrogen donor toward the ring-opened radical than is 1,4-cyclohexadiene, although both would be classed as relatively active hydrogen donors.

As mentioned above, conversion of the ring-cyclized radical $\underset{\sim}{9}$ to the dihydronaphthalene $\underset{\sim}{10}$ (and to other products such as tetrahydronaphthalenes and dimers) occurs principally via radical-radical termination reactions. Estimates of rate constants for such processes (ca. 10^9 M^{-1} sec^{-1}) indicate that under certain conditions a ring-cyclized radical might well still be around a second or more after the initial fragmentation.

Section Two – the section dealing with the evaluation of the mechanistic scheme – provides a considerable challenge because expressions for yields or ratios of products derived on the basis of a mechanism like that of Chart 1 are rather complex. In fact, no attempt was made to work out kinetic expressions until rather late in this work, for it

was expected that the derived expressions would be so complex as to be essentially useless. For the most part, kinetic treatments in the chemical literature and in text books which are applicable to problems involving reactive intermediates are restricted to cases wherein some function of observables (such as yields and ratios of products, reagent concentrations, the reaction temperature, and so on) can be put in linear form. Such treatments allow the success of a proposed scheme to be evaluated graphically by noting the scatter of points about a best straight line. In the present situation, however, it seems quite safe to say that no such linear relationships can be written.

A more versatile approach is clearly called for, and that taken here can be summarized by the statement that if an expression cannot be tested graphically, it may still be possible to do it numerically. In the approach used (26), an initial set of estimates for the parameters involved is iteratively refined in the sense of least-squares. In mechanistic studies, the parameters will usually be preexponential factors or activation energies for individual rate constants or, more commonly, for such combinations of rate constants as appear together in the mechanistic equations. The success of a candidate mechanism can then be judged in part by how well it can fit the experimental data. In addition, both the numerical values and the standard deviations of the parameters, which are also obtained, can be useful in assessing the reasonableness of the overall mechanism or of individual mechanistic steps. And as remarked earlier in this Overview, values for some of the parameters will be important for our understanding of the nature of the radical intermediates leading to the isomeric ring-opened and

ring-closed hydrocarbons.

A scientist's time is perhaps never better spent than in selecting systems for study, or in working out experimental procedures, which simplify matters to the extent possible. However, some things can be learned only in unavoidable complex situations, and in such cases numerical techniques can be indispensible. The computer exists, and the chemist should be prepared to use it. Perhaps publication of work such as this will help to acquaint others with the availability of numerical techniques for mechanistic studies.

In summary, the major part of this thesis will be concerned with the documentation of, and elaboration on, points raised in this Overview. In Section One we shall consider in detail the experimental observations and describe a possible mechanistic scheme. A general procedure for the numerical evaluation of a reaction mechanism will then be introduced in Section Two and applied to the present situation. Finally, the information on the behavior of the ring-opened and ring-closed radicals (or their equivalents) towards the hydrogen donors of interest will be drawn together in Section Three and discussed in the context of the general question of nonclassical free radical intermediates.

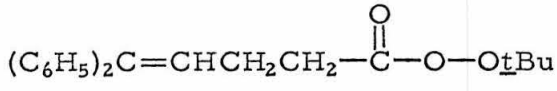
In view of the imposing length of this thesis, not at all accurately foreseen when the writing began, we have attempted to make the three Sections as independent as possible. We feel it should be possible for readers primarily interested in question of the nature of the radical intermediates to begin with Section Three, perhaps making use of the

abundant references to earlier discussions provided there whenever a strong urge is felt to check up on the support for assertions made in Section Three. Similarly, readers who are primarily interested in the procedure for the least-squares analysis might similarly begin with Section Two; those interested mainly in the results of that analysis may find it sufficient to read the first subsection and the five page summary of the fourth subsection of Section Two.

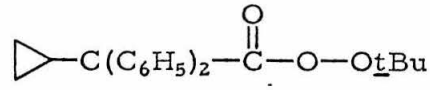
SECTION ONE: DEVELOPMENT OF A CANDIDATE REACTION MECHANISM

1. General Principles

In this section we shall develop a candidate reaction mechanism which assertedly can account in some detail for yields and ratios of reaction products observed for thermal decomposition under various conditions of t-butyl (γ,γ-diphenylallyl) peracetate (1) and t-butyl diphenylcyclopropylperacetate (2). Analysis of the quantitative success of the proposed mechanism in correlating relative yields of certain key products is undertaken in the next section.

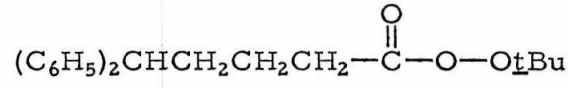


1



2

In addition, for reasons which will become apparent later, we will also be interested in the decomposition of 8, the saturated analog of 1.



8

Thermal decomposition of the peresters was chosen as the means by which to generate the radicals of interest in part for historical reasons (i. e., Howden (21) had previously employed 1) and in part for synthetic reasons (i. e., thanks to Maercker (69) and Bartlett (27), 2 could be made). Fortunately, this general method enjoys a substantial advantage over many of the other methods by which radicals of desig-

nated structure can be generated, such as the radical-chain decarbonylation of aldehydes, or the radical-chain reduction of halides by organotin hydrides. The advantage is that most of the main components defining the experimental conditions can be varied independently. For a given perester, those components can be taken to be (a) the identity and concentration of the hydrogen donor, (b) the reaction temperature, (c) the rate at which radicals are generated, and (d) the instantaneous perester concentration.

Of these, (a) has turned out to be perhaps the most important for this study. Changing the activity of the hydrogen donor enables one to study the pathways leading by hydrogen abstraction to product (as was stressed in the Overview for the relative formation of 1,1-diphenyl-1-butene and diphenylcyclopropylmethane). Changing the concentration and/or the identity of the hydrogen donor may be used to study partitioning between hydrogen abstraction and other types of reaction for radicals of interest (such as the k_a and k_r processes shown in Chart 1).

The factors (b), (c), and (d) in perester decompositions cannot be varied independently, however, for the reason that the values specified for any two suffice to determine that for the third. In particular, the rate of radical generation is given by the product of the rate constant for the decomposition (which, except for solvent effects (66), is determined by the reaction temperature) and the instantaneous perester concentration. Nevertheless, it will be useful to consider briefly mechanistic applications of all three. This is done in the next three paragraphs.

Variation of the reaction temperature will alter kinetic relation-

ships if various processes have different activation energies. If all rate constants can be described by the Arrhenius equation (67), product distributions will vary with temperature in a precise and ordered way, the details of which are fully determined by the assumptions made about the reaction mechanism. If the variations with temperature are found to hold to the expected pattern, the mechanism will be supported.

Of the many types of radical reactions, one which will always be present is bimolecular consumption of radical intermediates via disproportionation and/or combination reactions. Some products, then, will always be formed by reactions of pairs of radicals. If either member of a particular radical pair can be converted to product via pathways which do not involve a second free radical, the yield of the radical-radical product will depend on the steady-state radical concentrations. Formation of the ring-closed hydrocarbon, diphenylcyclopropylmethane, via disproportionation with cyclohexadienyl radicals (see Chart 1, page 17) is a case in point. Here, an alternative pathway for the ring-closed radicals is isomerization to ring-opened radicals, followed by the ortho-ring cyclization to the naphthalene series of products. Thus, we would expect that lower initial perester concentrations (which will lower the radical concentrations without changing temperature-dependent factors) should be associated with decreased yields of diphenylcyclopropylmethane. As Table 6 shows, such is indeed the case. On the other hand, if neither of the radical pair enjoys such options, a quite different result will be found; formation of the radical-radical product may take somewhat longer at lower steady-state radical concentrations, but will still get done. Thus, use of various initial

perester allows one to probe for the existence of certain options for particular radical intermediates.

As noted above, for a series of reactions at a common temperature, the steady-state radical concentrations will depend very substantially on the initial perester concentration. However, variation of the initial perester concentration can affect observed product distributions in ways other than the one suggested in the preceding paragraph. Specifically, only in the ideal situation will each molecule of reaction product survive the reaction conditions. In real situations, once-formed products are almost always themselves susceptible to attack by radicals which one would hope could only mind their business of forming primary reaction products. As a result, serious divergencies may arise between the observed product distributions and those which would be observed if each product molecule could be removed, as formed, to a safe place pending a final audit. Such divergencies can cause serious complications in making mechanistic analyses. The problem can usually be minimized (if the destruction of products is in fact due to radical attack) by using initial perester concentrations sufficiently low and hydrogen-donor concentrations sufficiently high that radical intermediates vent their fury entirely on the hydrogen donor. However, this procedure may introduce problems of its own; minor impurities in, or developed by, the solvent can loom large for very low initial perester concentrations. (For a practical example, see below, p. 116.)

In summary, the experimental conditions for decomposition of a given perester can be defined in terms of the solvent composition, the reaction temperature, and the initial perester concentration. The

effect of reasonably systematic variations in each of these factors has been investigated in this work.

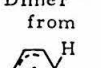
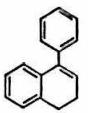
2. Yields and Ratios of Products

Nearly all of the experimental observations to be discussed in this thesis are summarized in the data tables which occupy the next several pages. For each table, the quantities defining the reaction conditions are given in the title and/or in the left-most columns. Observed yields of products are positioned toward the center, with product ratios, if displayed, toward the right. The tables are placed together, rather than being inserted as they are first referenced in the text, in order to make it easy for the reader to locate any given table and to most conveniently make comparisons between entries in different tables. In addition, some or all of the data has also been displayed graphically in Figures 1–4 which immediately follow Tables 1, 2, 3, and 10. Many readers will no doubt find the figures more instructive than the data tables.

A brief description of the general features of the experimental procedure is given in the following several paragraphs. Actually, there is no such thing as the experimental procedure. In view of this, additional information is recorded in the experimental section.

1. All reaction runs appearing in the tables were carried out on degassed samples in sealed tubes, immersed for ten or more half-lives in a bath containing an organic solvent of appropriate boiling point

Table 1. Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate at Approximately 0.26 M[a] in Solutions of 1,4-Cyclohexadiene in Cyclohexane.

Bath Temp., °C	[a]$_o$ M	Dimer[b,c] from 	yield, %										
			ϕ_2= 5	ϕ_2CH- 6	ϕ_2=[c,d] 13	A[c,d,e]	B[c,d,f]	 10	ϕ_2=  OtBu 12	Sub-Total	ϕ_2CH- 23	6/5	10 x [h]$_{av}$ 5
	1.11	0.06	9.0	0.30	0.8	2.0	9.7	20.1	20	62	13	0.033	2.01
	2.03	0.09	11.8	0.24	1.0	1.9	7.6	15.6	17	55	12	0.020	2.42
99	4.28	0.12	20.6	0.27	1.1	2.2	8.2	12.7	19	64	20	0.013	2.48
	4.28	0.11	19.7	0.26	1.3	2.6	8.4	13.8	17	63	--	0.013	2.86
	8.51	0.14	28.6	0.29	1.1	2.4	5.8	9.8	15	63	--	0.010	2.83
	1.08	0.08	9.5	0.49	1.0	2.1	13.6	25.7	17	70	--	0.052	2.53
131	1.98	0.09	14.4	0.40	1.1	2.3	12.1	21.8	19	71	18	0.028	2.74
	4.17	0.13	22.2	0.31	1.1	2.4	10.7	16.7	15	68	--	0.017	3.00
	8.28	0.17	30.4	0.33	1.3	2.8	9.5	11.6	15	71	--	0.011	3.14
	1.06	0.06	8.1	0.41	0.9	1.9	12.2	24.6	15	63	13	0.051	2.74
	1.94	0.07	13.7	0.44	1.0	2.4	15.6	22.7	17	73	--	0.034	3.07
150	4.08	0.10	21.7	0.43	1.2	2.3	11.5	17.5	12	67	12	0.020	3.16
	8.12	0.14	31.3	0.41	1.4	2.9	8.4	13.4	15	73	--	0.013	3.40
	8.12	--	31.5	--	1.0	2.6	10.0	13.5	13	71	--	--	3.41

[a] Assuming 12% volume expansion per 100° temperature rise. [b] mmoles per mmole perester taken.

[c] Equal moles of this material and 5 assumed to give equal vpc peak areas.

[d] Total for these three accurately known; separation into components approximately effected by triangulation.

[e] May be benzophenone; see text, pp. 121, 122. [f] Thought to consist of one or more isomeric 1-phenyltetrahydronaphthalenes; see pp. 77, 78.

[g] Tentatively identified; see Section One, subsection 6. [h] From Table 17, p. 297.

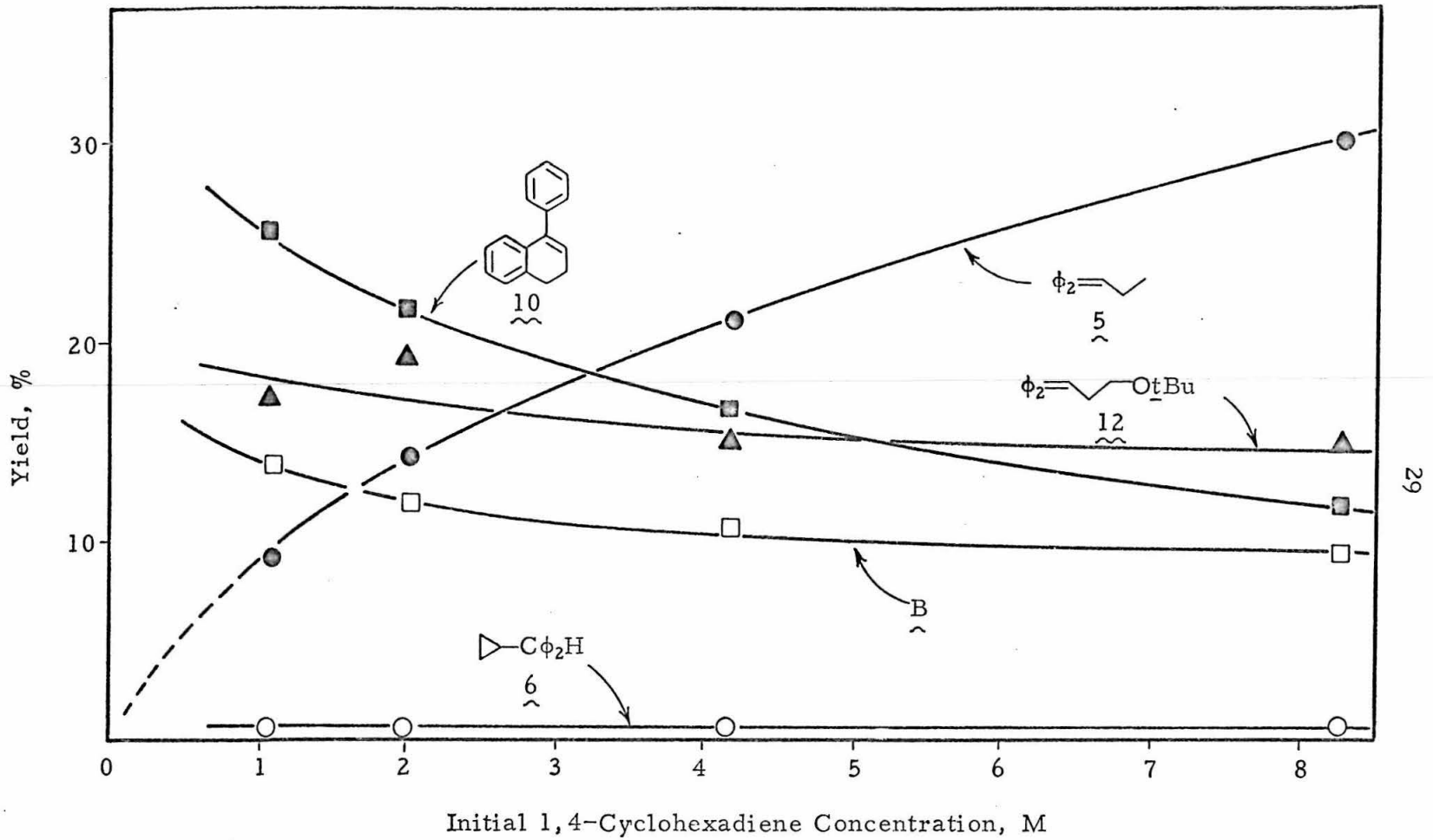
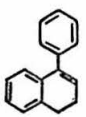


Figure 1. Thermal decomposition of t-butyl (γ, γ-diphenylallyl)peracetate (1) (0.26 M) at 131° in solutions of 1,4-cyclohexadiene in cyclohexane. Data from Table 1.

Table 2. Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate at 0.05 M[a] in Solutions of 1,4-Cyclohexadiene in Cyclohexane.

Bath Temp., °C	$[\bigcirc]_o$[a] M	Dimer[b] from 	Yield, % $\phi_2C{=}$ 5	ϕ_2CH- 6	B[c,d]	 10	Total[e]	6/5	10 × $[\bigcirc]_{av}$[f] / 5
0	2.95	0.10	18.9	13.5	40.0	12.0	84	0.715	1.87
	5.32	0.13	26.5	12.9	35.6	9.9	85	0.487	1.98
	7.97	0.16	33.7	13.2	35.5	9.6	92	0.392	2.27
	10.81	0.19	38.6	12.9	33.4	8.6	94	0.335	2.40
35	2.83	0.12	22.1	17.0	35.6	16.3	91	0.769	2.08
	5.11	0.15	31.1	16.1	30.9	13.6	92	0.518	2.23
	7.65	0.16	35.5	14.2	27.1	12.2	89	0.400	2.62
	10.38	--	45.0	14.6	28.0	11.0	97	0.325	2.54
70	2.72	0.12	19.8	15.1	31.0	20.4	86	0.763	2.79
	4.90	0.16	29.6	16.0	29.8	18.3	94	0.540	3.01
	7.34	0.13	35.8	14.5	26.0	14.4	91	0.405	2.95
	9.95	0.15	37.0	12.9	19.2	13.1	82	0.349	3.52

[a] Assuming 12% volume expansion per 100° temperature rise. [b] mmoles per mmole perester taken.

[c] Equal moles of this material and 5 assumed to give equal vpc peak areas.

[d] Ring-closed ether 15 plus diphenylmethylenecyclopropane 16 plus a third material thought to be the same as B in Table 1; see Section One, subsection 5B.

[e] Does not include 1-2% of a product which may be ring-opened ether 12 or para-t-butoxy ether 17; see text, pp. 76, 77.

[f] From Table 17, p. 297.

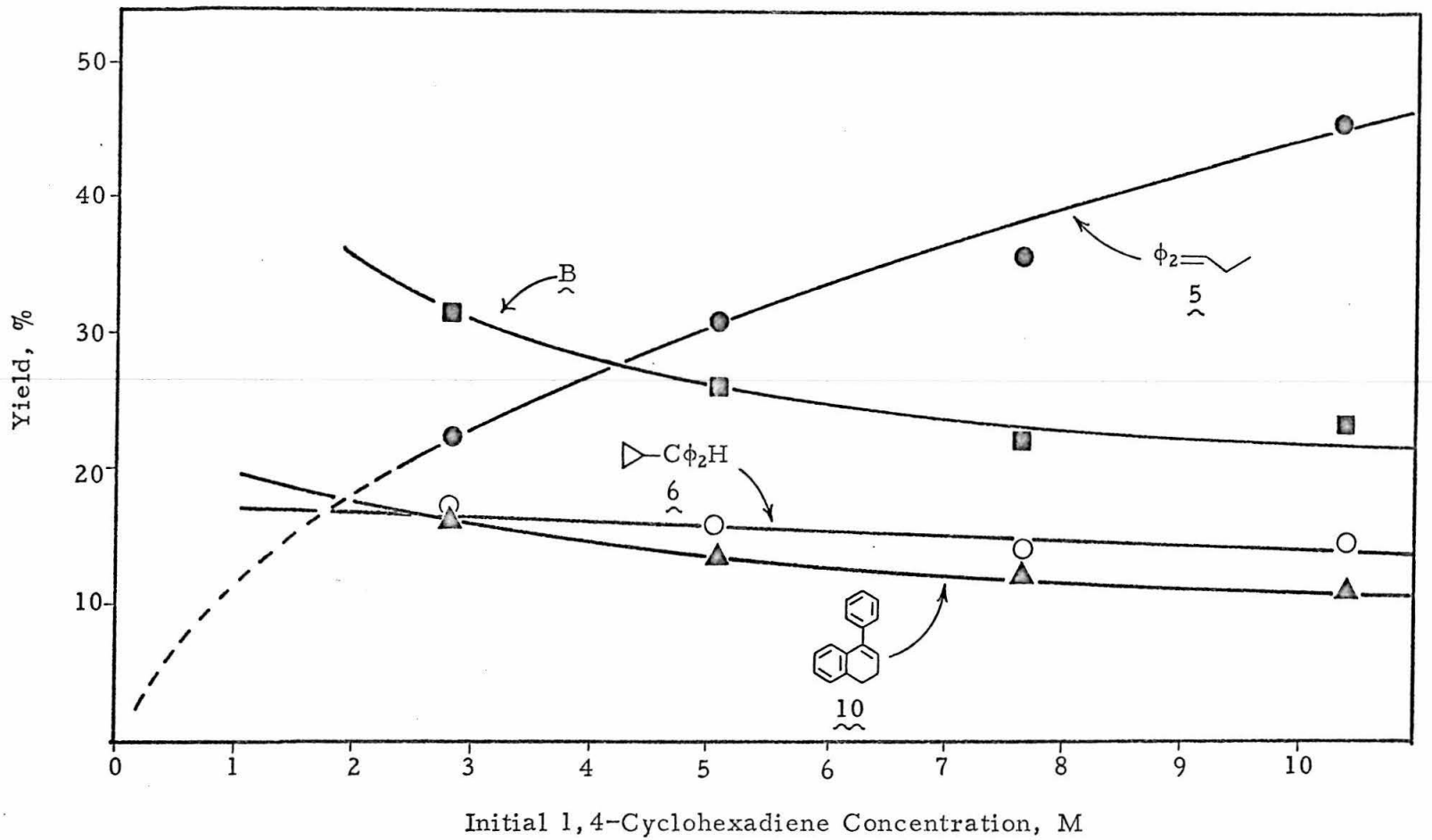
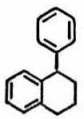


Figure 2. Thermal decomposition of t-butyl diphenylcyclopropylperacetate (2) (0.05 M) at 35° in solutions of 1,4-cyclohexadiene in cyclohexane. Data from Table 2.

Table 3. Thermal Decomposition at 152° of t-Butyl 5,5-Diphenylperpentanoate at Approximately 0.05 M in the Presence of 1,4-Cyclohexadiene and Cyclohexane.

[]$_M^a$	Dimer from  [b]	Yield, %[e]: ϕ_2 [d] 20	C [f]	 25	ϕ_2OtBu 18	Total	$25 \times [\text{}]_{av}$ / 20
0[c]	---	5.1	4.1	19.6	20	49	---
1.8	0.13	58	13.6	6.9	21	100	0.214
4.5	0.16	64	7.6	3.2	19	94	0.225
7.2	0.18	70	5.5	2.04	18	96	0.210
9.0	0.19	69	4.3	1.60	16	91	0.209

[a] Assuming 12% volume expansion per 100° temperature rise. [b] mmoles per mmole perester taken.

[c] Concentration of cyclohexane is 7.8 M[a].

[d] Corrected for assumed 2.0% yield of 4,4-diphenyl-1-butene; see p. 82.

[e] Yields calculated assuming hydrocarbon products have same vpc sensitivity as 1,1-diphenyl-1-butene and that the ether 18 has the same sensitivity as the ether 12.

[f] See pp. 141–144 for composition of C.

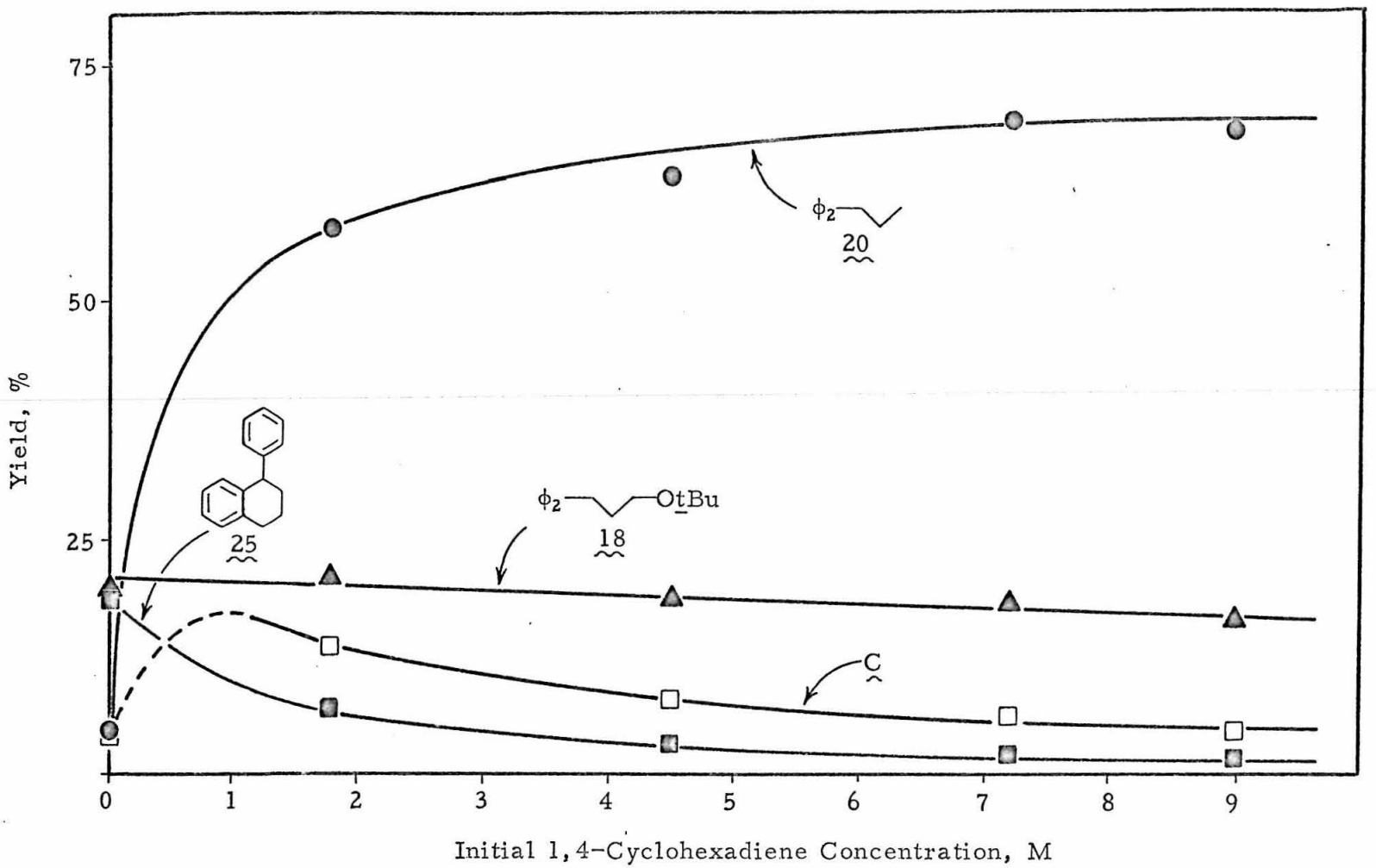
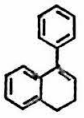


Figure 3. Thermal decomposition of t-butyl 5,5-diphenylperpropanoate (8) (0.05 M) at 152° in solutions of 1,4-cyclohexadiene in cyclohexane. Data from Table 3

Table 4. Thermal Decomposition at 110° of t-Butyl (γ, γ-Diphenylallyl)peracetate at Various Concentrations in Solutions of 1, 4-Cyclohexadiene in Cyclohexane.

Initial[a] Perester Conc., M	[⬡]$_o^a$ M	Yield, %										
		ϕ_2=⟨ 5	ϕ_2CH–◁ 6	ϕ_2=⟨^{b} 13	A[b,c]	B[b,d]	 10	ϕ_2=⟨–OtBu 12	Total[e]	$\frac{6}{5}$	$\frac{10 \times [⬡]^f_{av}}{5}$
0.27	1.11	6.7	0.30	0.5	1.8	5.5	17.7	16	49	0.044	2.43
0.030	1.22	9.7	0.19	1.6	3.6	13.4	22.7	21	72	0.020	2.79
0.030	1.22	9.5	0.20	1.5	3.5	12.3	22.0	20	69	0.021	2.79
0.0051	1.23	8.2	0.10	1.8	2.7	11.9	18.7	17	60	0.012	2.79
0.0010	1.23	9.9	0.11	2.1	2.9	13.1	19.7	18	66	0.011	2.46

[a] Assuming 12% volume expansion per 100° temperature rise.

[b] Total for these three accurately known; separation into components approximately effected by triangulation assuming equal moles of these materials and equal moles of 5 give rise to equal vpc peak areas.

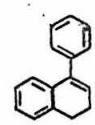
[c] May be benzophenone; see text, pp. 121, 122.

[d] Thought to be isomeric 1-phenyltrahydronaphthalenes; see text, pp. 77, 78.

[e] Also roughly 15–20% of a product at same retention time as that of material tentatively identified as lactone 23 in Table 1; see text, p. 85.

[f] From Table 17, p. 297. [g] Vessel packed with 100 mg glass wool in 2 ml of reaction mixture.

Table 5. Thermal Decomposition of t-Butyl (γ,γ-Diphenylallyl)-peracetate at Approximately 0.001 M in 1,4-Cyclohexadiene.

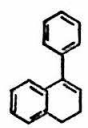
Bath Temperature °C	Initial[a] 1,4-Cyclohexadiene Conc., M	$\frac{\phi_2CH-\triangleleft}{\phi_2=\checkmark}$ [b]	$\frac{\text{  x [⬡]}_{av}}{\phi_2=\checkmark}$ [c]
99	9.65	0.0040	2.35
110	9.45	0.0036	2.70
125	9.34	0.0038	2.83
144	9.20	0.0037	--

[a] Assuming 12% volume expansion per 100° temperature rise.

[b] See text, pp. 116-118, 273-275.

[c] From Table 17, p. 297.

Table 6. Thermal Decomposition at 35° of t-Butyl Diphenylcyclopropylperacetate at Various Concentrations in Solutions of 1,4-Cyclohexadiene in Cyclohexane.

Initial[a] Perester Conc., M	$[\bigcirc]_o^a$ M	Yield, %							
		ϕ_2=⟨ 5	ϕ_2CH-◁ 6	ϕ_2=◁[b] 16	$B_2^{b,c}$	 10	Total[d]	$\frac{6}{5}$	$\frac{10 \times [\bigcirc]_{av}^{e}}{5}$
0.101	2.45	17.9	21.0	6.7	7.1	15.7	68	1.17	2.12
0.022	2.52	22.0	14.1	7.1	7.1	20.2	71	0.64	2.31
0.0060	2.53	28.5	10.0	8.0	6.5	23.6	77	0.35	2.09
0.0010	2.53	26.9	4.4	7.3	5.9	24.2	69	0.165	2.28

[a] Assuming 12% volume expansion per 100° temperature rise.

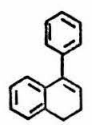
[b] Equal areas of this material and 5 assumed to give rise to equal vpc peak areas.

[c] Thought to be one or more isomeric 1-phenyltetrahydronaphthalenes; see text, pp. 77, 78.

[d] Does not include 1-2% of a product which may be ring-opened ether 12 or para-t-butoxy ether 17; see text, pp. 76, 77.

[e] From Table 17, p. 297.

Table 7. Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate (1) and t-Butyl Diphenylcyclopropylperacetate (2) in Indene at Approximately 0.05 M.

Perester	Bath Temp., °C	Initial[a] Indene Conc., M	Yield, % ϕ_2=⟨ 5	ϕ_2CH–◁ 6	ϕ_2=⟨// [b] 13	A[b,c]	B[b]	 10	ϕ_2=⟨–OtBu 12	Total	$\frac{10 \times [\text{Indene}]_{av}^{f}}{5}$
1	131	3.1[g]	6.2	≤ 0.06	≤ 0.1	0.2	0.4[d]	19.6	16	46	10
		7.5	10.7	≤ 0.02	≤ 0.1	0.3	0.5[d]	16.0	22	49	11
2	35	8.5	10.4	0.5	--	--	17.3[e]	11.2	--	39	9
			8.8	0.3	--	--	13.4[e]	12.7	--	37	12

[a] Assuming 12% volume expansion per 100° temperature rise.

[b] Equal moles of this material and 5 assumed to give equal vpc peak areas.

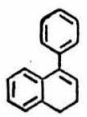
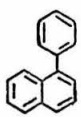
[c] May be benzophenone; see text, pp. 121,122.

[d] Thought to be one or more isomeric 1-phenyltetrahydronaphthalenes; see text, pp. 77, 78.

[e] Thought to be ring-closed ether 15 plus diphenylmethylenecyclopropane 16 plus isomeric 1-phenyltetrahydronaphthalenes; see Section One, subsection 5B.

[f] Initial indene concentration less initial perester concentration. [g] Cosolvent is n-octane.

Table 8. Thermal Decomposition of t-Butyl (γ,γ-Diphenylallyl)peracetate in Poorly Hydrogen-Donating Solvents and under Miscellaneous Conditions.

Solvent[g]	Temp., °C	Yield, %								
		ϕ_2=◇ 5	ϕ_2CH-◁ 6	ϕ_2=◇‖ [d] 13	A[d,e]	B[d,f]	 10		ϕ_2=◇-OtBu 12	Total
Cyclohexane	131[a]	1.0	0.11	0.0	1.0	2.7	26.5	5	14	50
Diethyl ether	131[a]	1.1	≤ 0.6[i]	0.0	1.1	2.5	31.5	2	9	48
Tetrahydrofuran	131[a]	1.0	0.05	0.0	1.3	1.0	15.6	1	9	29
Cumene	150[a]	1.3	0.2	-	-	-	-	-	-	-
1,4-Cyclohexadiene, 0.2 M in n-octane	110[b]	2.4	0.12	1.4	2	7	24.3	-	13	49
1,4-Cyclohexadiene	150[a,j]	31.6	-	0.8	1.3	10.6	12.4	-	14	71
1,3-Cyclohexadiene, 0.6 M, in 1,4-Cyclohexadiene	150[a]	33.8	-	1.0	1.5	10.8	15.9	-	15	78
1,4-Cyclohexadiene, 0.85 M in Methanol	100[c]	0.7	0.1	0.03	0.1	0.3	2.9	-	1.1	5[h]

Footnotes for Table 8

[a]Initial perester concentration ca. 0.25 M.

[b]Initial perester concentration ca. 0.01 M.

[c]Initial perester concentration 0.11 M.

[d]Total for these three reasonably accurately known; separation into components approximately effected by triangulation assuming equal moles of these materials and equal moles of 5 give rise to equal vpc areas.

[e]May be benzophenone; see text, pp. 121, 122.

[f]Thought to be isomeric 1-phenyltetrahydronaphthalenes; see text, pp. 77, 78.

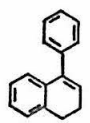
[g]Solvent concentrations quoted assume a volume expansion of 12% per 100° temperature rise.

[h]Also several new products; see Section One, subsection 6.

[i]See text, p. 130.

[j]Reaction time 6 hr; analogous runs in Table 1 (i.e., rows 13 and 14) used reaction times of 2 hr.

Table 9. Thermal Decomposition of t-Butyl Diphenylcycloproplyperacetate in Poorly Hydrogen-Donating Solvents.

Solvent	Bath Temp., °C	Initial Perester Conc., M	Yield, %					$\frac{6}{5}$	$\frac{5}{10}$
			ϕ_2=◁ 5	ϕ_2CH–◁ 6	B[a,b]	 10	Total		
Cyclohexane	35	0.25	1.0	8.7	15	17.5	42	8.7	0.057
	35	0.05	1.1	7.5	27	23.5	59	6.8	0.047
	70	0.05	1.1	7.7	23	27.0	59	7.0	0.041
	35	0.01	0.5	3.4	19	17.3	40	6.8	0.029
Diethyl-ether	0	--	1.5	8.3	10	18.1	38	5.5	0.083
	35	0.05	2.0	9.5	15	28.0	55	4.7	0.071
	70	--	1.6	7.8	12	27.3	49	4.9	0.059
Benzene	35	0.2	0.4	9.1	8	9.4	28	25	0.04
		0.05	1.1	11.5	17	18.5	48	10	0.06
Et_4SnH	35	0.01	0.5	1.6	20	17	39	3.2	0.03

[a] Equal moles of this material and 5 assumed to give equal vpc peak areas.

[b] Thought to be ring-closed ether 15 plus diphenylmethylenecyclopropane 16 plus one or more isomeric 1-phenyltetrahydronaphthalenes; see Section One, subsection 5B.

Table 10. Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate (0.002 M unless otherwise noted) in Solutions of Triethyltin Hydride in n-Octane.

Bath Temp., °C	$[Et_3SnH]_o$[a] M	Yield, %									
		$\phi_2C{=}CH{-}CH_2{-}$ 5	$\phi_2CH{-}$ 6	B[b,c]	10	Total Hydrocarbons	$\phi_2C{=}CH{-}CH_2{-}OtBu$ 12	Tin[d] Ester 14	Total	5/6	$10 \times [Et_3SnH]_{av}$ / 5
110	0.011	3.3	0.24	13	17.0	34	3.3	44	81	14	0.051
125	0.011	2.9	0.17	12	18.5	34	3.9	--	--	17	0.064
	0.044	11.1	0.76	(8)[i]	15.6	36	4.0	(49)[h]	(89)	15	0.059
	0.140	23.5	1.63	(4)[i]	10.0	39	2.0	--	--	15	0.059
	0.39	28.2	2.28	(2)[i]	3.6	36	0.7	(40)[h]	(86)	12	0.050
	0.94	30.7	2.85	--	1.4	35	≤ 0.25	--	--	11	0.046
144	0.047	10.5	0.66	10	18.5	40	3.3	--	--	16	0.079
	0.141	16.8	0.97	4	10.1	32	1.9	--	--	17	0.083
	0.38	19.6	1.41	2	3.6	27	0.6	--	--	14	0.070
	0.93	11.2	1.33	--	0.3	13	< 0.2	--	--	9	0.024
125[e]	1.34	34.1	2.9	--	1.1	38	< 0.2	~50	~90	12	0.04
131[f]	1.89	34.3	2.2	--	0.6	37	< 0.2	--	--	17	0.03
110[g]	0.74							49			

[a] Assuming 12% volume expansion per 100° temperature rise.
[b] Thought to consist of one or more isomeric 1-phenyltetrahydronaphthalenes; see text, pp. 77, 78.
[c] Equal moles of this material and 5 assumed to give rise to equal vpc peak areas.
[d] $\phi_2C{=}CH{-}CH_2{-}CO_2SnEt_3$.
[e] Initial perester conc. 0.12 M.
[f] Initial perester conc. 0.05 M.
[g] Initial perester conc. 0.02 M.
[h] Measured at 110°.
[i] See text, p. 134.

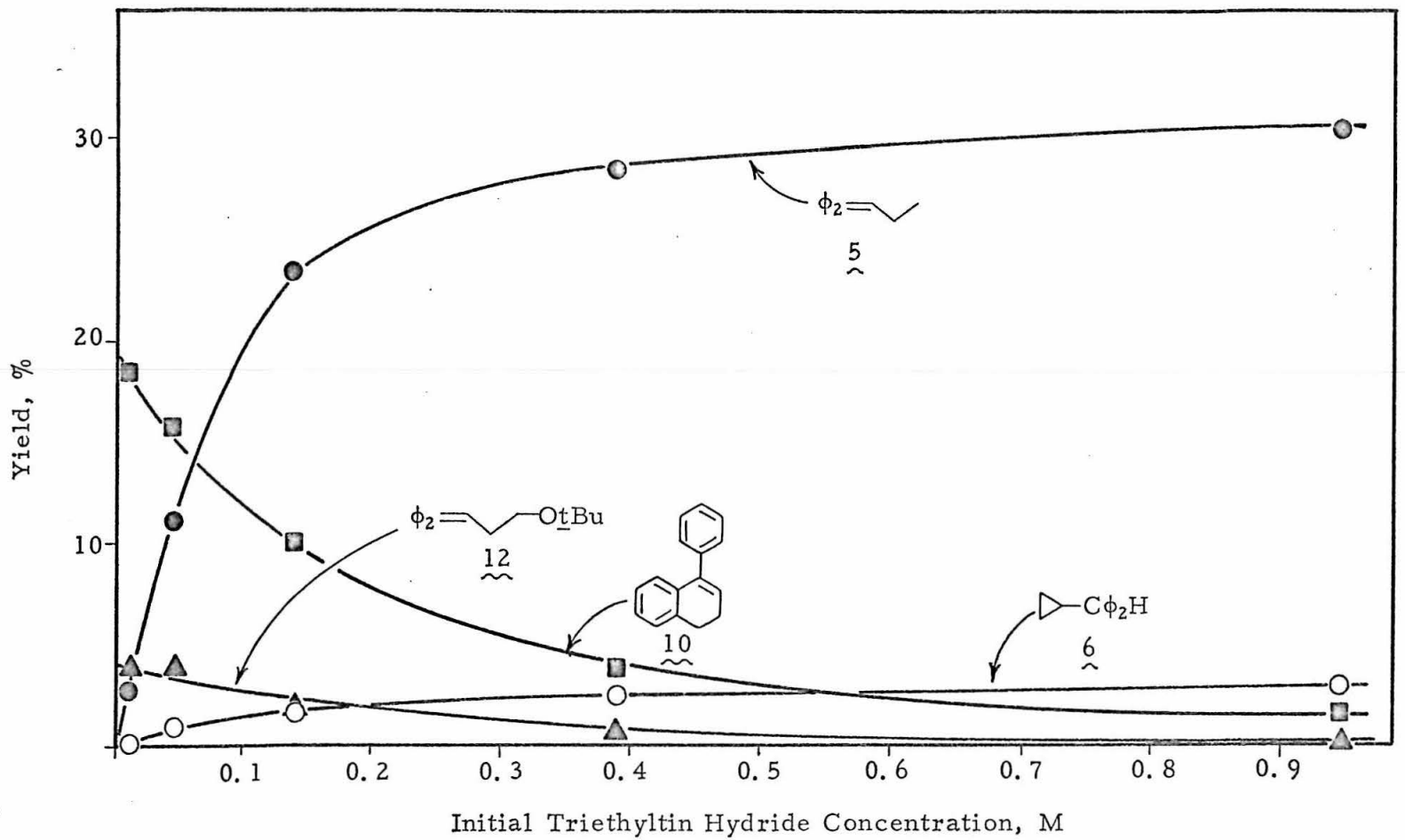


Figure 4. Thermal decomposition of t-butyl (γ, γ-diphenylallyl)peracetate (1) (0.002 M) at 125° in solutions of triethyltin hydride in n-octane. Data from Table 10.

Table 11. Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate in the Presence of Triethyltin Hydride.

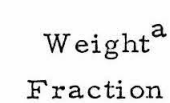
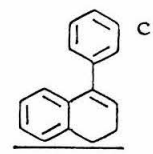
Bath Temp., °C	Initial Perester Conc., M	Initial Et_3SnH Conc., M	Yield, %				$\frac{6}{5}$	$\frac{10 \times [Et_3SnH]_{av}^{d}}{5}$
			ϕ_2=  5	ϕ_2CH-  6	 10	Total[c]		
10[a]	0.020	1.02	(Absolute Yields Not Determined)				0.39	0.037
		2.04					0.45	0.048
		3.06					0.54	0.074
		5.1					0.76	0.11
35[b]	0.010	0.25	62	10	4.4	76	0.16	0.017
		0.6	65	12	1.8	79	0.19	0.016
		1.8	68	16	1.0	85	0.24	0.026
		4.8	62	23	0.7	86	0.37	0.006

[a]Co-solvent is benzene. [b]Co-solvent is n-octane.

[c]Does not include any B that may be formed; see text, pp. 80, 81.

[d]Initial Et_3SnH concentration less initial perester concentration.

Table 12. Product Ratios Observed by Howden (21) for Thermal Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate at 0.056 M in the Presence of Tri-n-butyltin Hydride

Bath Temp., °C	$[Bu_3SnH]$ M	Solvent	Weight[a] Fraction Hydrocarbon Isolated	Percent[b] CO_2 Evolved		
110	0.056	C_6H_5Cl	0.15	51	22	1.52
110	0.28	C_6H_5Cl	0.15	44	20	0.12
110	0.28	Cumene	0.50	36	17	0.12
110	0.56	C_6H_5Cl	0.33	73	17	0.06
130	0.28	Cumene	0.36	58	18	0.2
150	0.112	o-$C_6H_4Cl_2$	0.53	73	--	1.2
150	0.28	Cumene	0.41	80	20	0.12

[a]By distillation. [b]From total gas evolution assuming only carbon dioxide is evolved. [c]Obtained from Howden's vpc traces by triangulation assuming that a peak at the proper retention time for the dihydronaphthalene 10 is due to that material.

at reflux or otherwise subject to temperature control.

2. Yields and ratios of various products were obtained, except where noted, by vapor-phase chromatography (vpc) on a Perkin-Elmer Model 800 Gas Chromatograph equipped with a flame-ionization detector. Unless otherwise specified, the column employed was 6-12 ft. ($\frac{1}{8}$ in. o. d.) of aluminum tubing packed with 10% Ucon polar HB 5100 on 80-100 mesh HMDS treated Chromasorb W. In the usual procedure, area measurements relative to added internal standard (either diphenylmethane or 1-phenylnaphthalene) were made using a Perkin-Elmer Printing Integrator. However, triangulation, peak cut-out weights, or peak-height analysis were employed where baseline instability or inadequate resolution made the alternative procedures necessary or preferable. The relative areas were then converted to percentage yields for the various products from the weights of perester and internal standard taken and relative response factors, if known. Where the response factor is unknown (which is the case for several products not isolated in pure form), the assumption has been made that equal weights of 1, 1-diphenyl-1-butene (5) and of the product in question give rise to equal peak areas. Except for the runs at 10° in Table 11, the internal standard, if any, was added after completion of the thermal decomposition.

3. In most cases the vpc analysis was made on the crude reaction mixture (plus internal standard) itself. For reaction series featuring runs below about 0. 05 M initial perester concentration or in the presence of triethyltin hydride, however, it was necessary to concentrate the reaction mixture to prevent interference of the solvent peak

with the vpc analysis.

4. As will become evident, one or more spurious (i. e., incompletely characterized) factors seem to be operative in the decompositions of the ring-closed perester 2. Therefore, runs using 2 from common perester preparations will be so identified in the experimental section.

A few comments are now offered concerning the accuracy of the tabulated data. These comments should be taken into account in deciding whether observed trends are real or likely to be artifacts of the experimental procedure. We have previously discussed one reason--destruction of primary reaction products--that observed yields may not correspond precisely to amounts of products formed. Two others of experimental origin are: (a) error in the vpc area measurements. In most cases, reported yields are based on three or four vpc determinations. Nonetheless, relative observed yields or product ratios may be off by up to five percent even where no problems of resolution were encountered. Where such problems were encountered (see below), a much higher figure may be appropriate; and (b) in general, weights of perester, in the amount of about 20 mg, was weighed directly. If that weight is taken to be good to ± 1 mg, absolute yields will be uncertain to five percent over and above the uncertainty due to the relative-area measurements. In addition, uncertainty in the weight of internal standard taken can also often contribute an appreciable uncertainty in the product ratios. Note, however, that this weight-uncertainty factor does not effect ratios of products taken within a given run (such as the

figures in the right-most columns of the data tables). For this reason, we will be on safer ground in working with these quantities, and it will be better to test a reaction mechanism by how well it reproduces ratios of products than by how well it does on absolute yields.

Consider, for example, the yields of the various products quoted in Table 2 for decomposition of the ring-opened perester 1̂ in the presence of 1,4-cyclohexadiene. For the three runs at about 1 M initial cyclohexadiene concentration, the one at the intermediate temperature (131°) gave the highest yield for all but one of the several products. It is no mean task to conceive of a mechanism which will reproduce such a pattern. In general, one would expect a monotonic variation with temperature, although a maximum yield at an intermediate temperature might be found for a given product if two or more mechanistic pathways to that product were properly combined or if product destructions had different temperature coefficients. In the case in question, however, the observed pattern is almost surely artificial.

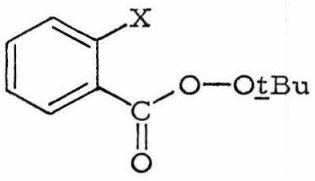
The reader is advised that absolute yields are probably always reported to more precision than combined weight-uncertainty and area-uncertainty factors would support, in order to facilitate the calculation and comparison of product ratios.

3. Mechanisms of Perester Decompositions

Unimolecular homolytic decomposition is the most common, but not the only, mechanism by which t-butyl peresters have been known to decompose. Alternative mechanisms include heterolytic decompo-

sition, ionic decomposition catalyzed by strong acid, radical-induced decomposition, and molecule-induced decomposition. Rüchardt has supplied a comprehensive review of the mechanism of perester decompositions (7). Of the types listed above, homolytic, radical-induced, and molecule-induced decompositions have been observed in the present research.

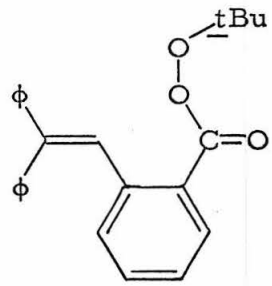
Let us take up these three mechanistic possibilities in reverse order. Molecule-induced decomposition (if intramolecular) is the free-radical analog of the neighboring-group participation in ionization which is so well known in carbonium ion chemistry (8, 28). The ortho-substituted t-butyl perbenzoate system employed by Martin and co-workers (29) is the free-radical system which seems to have been the most extensively studied. Although the immediate products of the induced decomposition are free radicals (a cyclized lactone radical and a t-butoxy radical), the large solvent effect on reaction rate observed by Martin

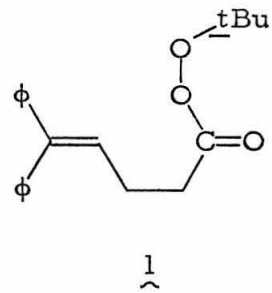


$$X = \left\{ \begin{array}{l} -I \\ -CH{=}C(C_6H_5)_2 \\ -SC_6H_5 \\ -SCH_3 \end{array} \right\}$$

indicates that the decomposition transition state apparently enjoys substantial ionic character.

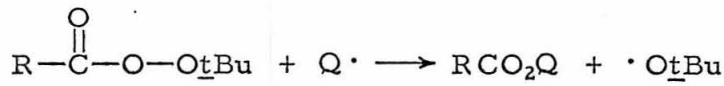
The case where X = diphenylvinyl is especially relevant here because of the strong structural similarity of that perester to the ring-opened perester 1.





1

Two types of radical-induced decompositions are known. One simply consists of attack by a radical (Q· in the below) at one of the peroxy oxygens. The process shown might be called "acyloxy-group



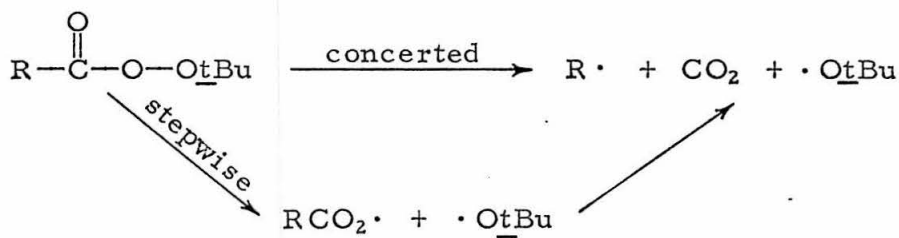
abstraction" to emphasize its formal similarity to the perhaps more familiar "hydrogen atom-abstraction" reaction. Radical attack on the other peroxy oxygen to give ether and an acyloxy radical, $RCO_2\cdot$, is also conceivable. The second type of radical-induced decomposition involves the establishment of a radical center within the perester molecule, usually via abstraction of a hydrogen atom from the perester (7); the newly established radical center may then intramolecularly attack the peroxy-oxygen linkage to give the cyclic ester and a t-butoxy radical (7).

Radical-induced decomposition is the predominant mechanism for decomposition of the ring-opened perester 1 (and possibly for the isomeric ring-closed perester 2) in the presence of triethyltin hydride under conditions employed in this work. This apparently is the first

case in which a radical-induced perester decomposition involving attack on the peroxy functionality has been documented by product isolation as well as by kinetic evidence.

Under all other conditions investigated in this work, radical-induced decomposition appears to be negligible or absent.

Two mechanisms are conceivable for the normal homolytic decomposition. The two bonds broken in the overall process may cleave simultaneously with expulsion of carbon dioxide, or the weaker oxygen-oxygen bond may cleave first, followed by decarboxylation of the resulting acyloxy radical:



Bartlett and Hiatt (30) employed the following reasoning in attempting to distinguish in particular cases between the two possibilities. If the decomposition is concerted, the stability of the radical R· should strongly influence the rate of decomposition. On the other hand, the nature of the R group should have little effect on the stability of an acyloxy radical, and hence on the rate of decomposition, if the decomposition is stepwise. Table 13 lists half-lives at 110° for a series of peresters, many of which were studied by Bartlett and Hiatt. The variation in the ratio of the half-lives by a factor of 4×10^4 from the fastest to the slowest is a major change in most leagues, and can hardly mean other than that the decomposition is concerted, at least

Table 13. Half-Lives for Thermal Decomposition of Peresters, $R-CO_2-OtBu$, in Chlorobenzene at 110°.

R-Group	Half-life, min.	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, e.u.	Ref.
CH_3-	230[c]	38	17	31
$(C_6H_5)_2CHCH_2CH_2CH_2-$	210	--	--	21
$(C_6H_5)_2C=CHCH_2CH_2-$	150	--	--	21
$CH_3(CH_2)_7CH_2-$[a]	139	35.3	14.0	22
$CH_3(CH_2)_{10}CH_2-$[a]	133	35.0	13.1	22
endo-norbornyl-	26	35.6	16.4	10
exo-norbornyl-	20	30.9	6.7	10
cyclohexyl-	14	31.3	8.6	10
$(CH_3)_2CH-$	135[b]	31.8	9.4	32
$C_6H_5CH_2-$	5.9[c]	28.7	4	33
$(CH_3)_3C-$	0.89[b]	30.0	11.1	33
$C_6H_5CH=CHCH_2-$	0.8[c]	23.5	- 6	30
$(C_6H_5)_2CH-$	0.18[c]	24.3	- 1	30
$C_6H_5(CH_3)_2C-$	0.06[c]	26.1	6	30
$(C_6H_5)_2CH_3C-$	0.04[c]	24.7	3	30
$C_6H_5(CH=CH)CH-$	0.025[c]	23.0	- 1	30
$(C_6H_5)_3C-$	0.006[c]	24.1	4.9	27

[a] Half-lives are for chlorobenzene but activation parameters are for nitrobenzene.

[b] Calculated by the Arrhenius relationship using authors' rate constants.

[c] Extrapolated (Eyring equation) from the half-life at 25 or 60° and enthalpy of activation quoted in the reference listed.

for those R-groups in the lower half of the table (30).

The interesting question is whether all of the peresters undergo concerted decomposition, or whether the slower ones decompose sequentially, with a change in mechanism occurring somewhere along the line; and if the latter is the case, where does the change occur?

To make a comparison between radical stabilities and decomposition rates we need some measure of the former. A reasonable procedure would be to use C-H bond-dissociation energies where these are available. Unfortunately, the requisite dissociation energies are available for only a few of the groups listed in Table 13. However, a scale can be constructed for the simple aliphatics; and the fact that the perester with R equals t-butyl decomposes about 250 times as rapidly as the parent perester with R equals methyl, suggests that the change in mechanism, if one occurs, will be found within that series. (For convenience we shall refer to a perester by giving the identity of the R-group.) Following Walling (34) we assign stabilization energies relative to methyl of: 4 kcal/mole for a primary radical; 8 kcal/mole for isopropyl or other unstrained secondary radical; and 12 kcal/mole for the t-butyl radical. Thus, the increment in stability is essentially constant in going from methyl to primary, from primary to secondary, and from secondary to tertiary.

If, then, all of the aliphatic peresters decompose concertedly, the half-lives should show a geometrical progression. That is, we should have approximately (ethyl/methyl)^3 = (isopropyl/methyl)^2 = (t-butyl/methyl); or t-butyl/isopropyl = isopropyl/ethyl, etc. From Table 13 we see that t-butyl decomposes about 15 times as rapidly as

isopropyl or cyclohexyl and that the unstrained secondary aliphatics decompose about 10 times as rapidly as those with primary R-groups. Thus, the decomposition is almost certainly concerted when R· is at least as stable as a secondary aliphatic radical.

However, the primary aliphatics decompose only about 50% faster than the parent perester, t-butyl peracetate. If we were quite certain that substitution of n-alkyl for methyl should not change the rate constant for simple oxygen-oxygen scission by more than some few percent, the slight rate acceleration observed could be taken as evidence that peresters with primary R-groups decompose partly by the concerted and partly by the sequential mechanism. Lacking that degree of confidence, we can only suggest here that a combination of concerted and stepwise processes is an attractive possibility for peresters such as ring-opened perester 1.

We might also mention another important factor in perester decompositions first identified by Bartlett and Hiatt (30). This factor concerns the lower entropies of activation observed where the radical R· can be stabilized by resonance. Effective resonance stabilization, as is well known, requires that the radical assume an optimal configuration with respect to rotation about one or more bonds. A partial freezing out of the same rotation(s) should be required if resonance stabilization of the incipient radical is to be available at the transition state, and the freezing out in the transition state of rotations allowed in the perester itself results in a lowered entropy of activation.

Bartlett and Hiatt pointed out that the trend is so well obeyed that

the entropies of activation fall into a number of ranges associated with the number of frozen rotations (30). For isopropyl or t-butyl, where rotation about one bond must be fixed in developing the molecule of carbon dioxide, the entropy of activation is 9 e.u. or greater. For benzyl and cumyl, the orientation of the phenyl ring must also be properly set, and the entropies of activation are 4 and 6 e.u., respectively. Entropies of activation are 3 e.u. for diphenylethyl, -1 e.u. for diphenylmethyl, -1 e.u. for phenylvinylmethyl, and -6 e.u. for cinnamyl; all cases in which 3 bonds must be properly oriented at the transition state.

The one significant deviation from the pattern occurs for triphenylmethyl, whose activation parameters were only recently reported by Lorand and Bartlett (27). The reasoning employed above would suggest frozen rotations for 4 bonds in triphenylmethyl and a negative entropy of activation. The actual value, however, is about +5 e.u. The authors suggest that steric crowding in the 'tetrahedral' perester might be relieved as the triphenylmethyl group approaches the trigonal geometry of the radical; this factor would clearly tend to increase the entropy of activation. In addition, the steric congestion may orient the phenyl groups in the perester itself in a propeller configuration similar to that postulated for the triphenylmethyl radical (68). Thus, the increase in orientation at the transition state might be rather small.

This discussion is intended to convince (or to remind) the reader that the correlation of structure with activation parameters is sufficiently well advanced for perester decompositions to allow the estimation of

activation parameters in new cases (e. g. , the isomeric peresters 1 and 2). The reason is that activation parameters for the isomeric peresters will have to be specified in Section Two to quantitatively test the mechanism outlined in the present section, and those parameters have not been determined experimentally. As some rate information is available for each of the peresters, however, the procedure adopted is not thought to seriously compromise the mechanistic evaluation.

4. Cage-Reaction Processes - A general Discussion

Cage-reaction processes may occur when homolytic cleavage of one or more bonds creates a pair of reactive intermediates. If the reaction takes place in the gas phase at pressures of less than tens of atmospheres (35), the particles tend to diffuse apart so rapidly that there is no significantly greater chance that each will react with its original partner than with some species produced in a neighboring decomposition. In solution, however, the surrounding solvent molecules can greatly slow the separation of the radical pair. There is then in effect a solvent cage (36) about the particles which may allow a considerable number of radical-radical encounters before diffusion occurs to give separated radicals. In the course of their movements within the solvent cage, the original partners may (re)combine or disproportionate.

Cage reactions may be studied experimentally by determining the influence of added radical scavenger on the product distribution (24, 37). The idea is that reaction in the solvent cage is likely to take place very soon after the fragmentation, whereas products arising from reactions

between radicals from separate decompositions are formed relatively later because of the requirements for diffusion. A scavenger of appropriate reactivity could then suppress the non-cage processes while leaving the cage processes essentially unaffected. And if the characteristic times for the two types of processes differ by several orders or magnitudes, a clean separation should be possible.

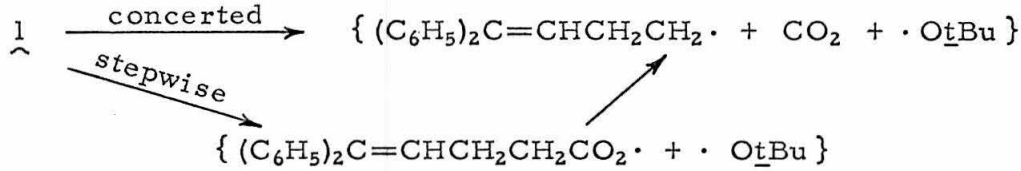
Moreover, experiments with very active scavengers have shown that at sufficiently high scavenger concentrations, the cage process itself can be interdicted (24, 37). In the present work, however, none of the solvents employed seems to react with any of the species directly produced by decomposition of either the peresters on a time scale as short as that which describes the cage processes, and no experiments with specially added radical scavengers have been carried out.

Just what is the time scale for cage processes observed in this work cannot be said with certainty. However, Noyes has suggested that in ordinary solvents the competition between cage reaction and diffusion will normally allow about 10^{-9} seconds for the former to be effected (24). Of course, the actual figure will vary with the nature of the caged particles, with the properties of the solvent, and with other factors, but Noyes' estimate should at least allow us to place upper limits on the rate constants for certain reaction steps.

5. Cage Processes in Decomposition of the Peresters

A. t-Butyl (γ,γ-Diphenylallyl)peracetate

Table 13 shows that the ring-opened perester 1 decomposes at 110° at a rate appropriate for a perester giving a primary radical. Moreover, the discussion in subsection 3 suggested that such peresters may decompose by a combination of concerted and stepwise pathways, as illustrated below for the ring-opened perester:



11

If the decomposition were entirely stepwise, the acyloxy radical would have to rapidly decarboxylate in the solvent cage to account for cage products observed and reported below. That this might well be possible is suggested by the work of Braun, Rajbenbach, and Eirich (38) who have shown that decarboxylation of acetoxy radicals (from the thermal decomposition of acetyl peroxide) is competitive with diffusion from the solvent cage. As acyloxy radicals have apparently not been trapped in this work, however, it will be sufficient to consider, for the present at least, that by some combination of the two pathways caged pairs consisting of a ring-opened radical 3 and a t-butoxy radical are generated.

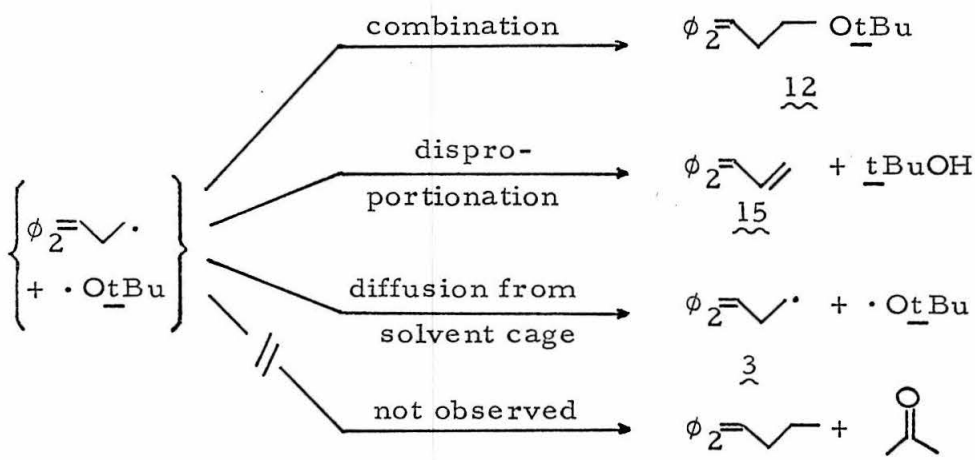
We will consider first the formation of cage products in ether and hydrocarbon solvents. Then we will note how the pattern is changed in

the presence of triethyltin hydride, where induced decomposition of 1 by triethyltin radicals competes with the normal process.

(1.) In Hydrocarbon and Ether Solvents

Of the several types of cage processes which might be considered, definite evidence was obtained for coupling to diphenylbutenyl t-butyl ether, 12, and disproportionation to 1,1-diphenyl-1,3-butadiene, 13, plus t-butyl alcohol. Because t-butoxy radicals undergo β-scission (to yield a methyl radical plus acetone), the disproportionation-type reaction shown lowermost below was considered, but ruled out when careful vpc analysis failed to detect 1,1-diphenyl-1-pentene for decomposition of 1 in 1,4-cyclohexadiene, cyclohexane, or diethyl ether.

Chart 2. Cage Reactions in the Thermal Decomposition of t-Butyl (γ,γ-Diphenylallyl)peracetate.



The ether 12 was detected by vpc for decomposition of 1 in 1,4-

cyclohexadiene, cyclohexane, indene, diethylether, and tetrahydrofuran (Tables 1, 3, 7, 8). No assay was made for the run in cumene listed in Table 8. It can be separated conveniently from the other reaction products by elution chromatography on florisil or alumina. A separated sample from a run in the presence of 1,4-cyclohexadiene gave a nmr spectrum which agreed with that of the authentic material

The identification of the diene is somewhat less well established. Maercker and Roberts (69) found that the dialkylmercury compound shown below decomposed during attempted distillation under reduced

$$[(C_6H_5)_2C{=}CHCH_2CH_2]_2Hg \xrightarrow[0.05\ mm]{250^\circ} (C_6H_5)_2C{=}C{-}CH{=}CH_2 + (C_6H_5)_2C{=}CHCH_2CH_3 + \text{indene} + \text{indene} + Hg$$

13 (35%); 5 (35%); 10 (28%); (trace)

pressure to give a distillate containing metallic mercury and a 1:1 mixture of ring-opened hydrocarbon 5 and a compound which from its nmr spectrum was tentatively identified as the diene 13. The retention time of the diene 13 relative to 5 on the standard Ucon Polar column appears to be the same as that of the peak attributed to 13 in this work. The diene 13 may well have been formed under Maercker's conditions by thermal decomposition of the mercury compound in the distillation pot followed by disproportionation of the caged diphenylbutenyl radicals. Dimerization would be expected as well, but only the monomeric products would have distilled.

Evidence that the ether 12 and the diene 13 are in fact cage pro-

ducts is offered in the next several paragraphs in the context of how one might in general attempt to distinguish cage products from products formed in other ways.

Yields of the ether 12 are given in Table 1 for decomposition of 1 at approximately 0.25 M in the presence of 1,4-cyclohexadiene. The major point to be noted is that the yield of the ether is substantially independent of the cyclohexadiene concentration. In this case, 1,4-cyclohexadiene scavenges radical pairs which escape the solvent cage. Thus, the constancy of the yield at any given temperature is consistent with a cage-reaction origin of 12. However, constancy of yield is not a sufficient criterion. For example, the yield of diphenylcyclopropylmethane, 6, also varies little with the 1,4-cyclohexadiene concentration (Table 1). Yields of the same material from the isomeric ring-closed perester 2 (see Table 2) show a similar constancy. Nevertheless, we shall see shortly that 6 is not in fact a cage product.

As was pointed out in subsection 1, yields of radical-radical products may in some cases depend strongly on the steady-state radical concentrations, which in turn can be rather uniformly varied by varying the initial perester concentration. However, the yields of cage products will not depend on the steady-state radical concentrations, for both radicals come from the decomposition of a single perester molecule. Some variation of yield with perester concentration may still be possible, however, for two reasons: (a) as also discussed in subsection 1, destruction of primary products will, if anything, be more important at higher perester concentrations; and (b) if induced decomposition (which gives no cage product) competes with the normal decomposition,

the relative amount of the latter will usually be greater at lower perester concentrations (39).

The concentration study of Table 4 shows that the yield of the ether 12 is substantially independent of the initial perester concentration, although the data are rougher than one might like. Note, however, that the yield of the hydrocarbon 6 varies by a factor of four. A similar variation with perester concentration is seen in Table 6, where the perester employed is 2. Thus, 6 cannot be a cage product.

Again, the lack of a concentration dependence is not a sufficient criterion. For example, the yield of the ring-cyclized hydrocarbon 10 (see Table 4 or Table 6) is not greatly dependent on the initial perester concentration, and even rises slightly at lower perester concentrations, as we have noted a cage product might. However, we can be sure that 10 is not a cage product because it fails the first test--invariance of the yield on the 1,4-cyclohexadiene concentration (see Table 1)--and because the ring-cyclization can be easily shown to be orders of magnitude too slow to compete with diffusion of the ring-opened radical from the solvent cage.

The ring-opened ether 12 passes both the scavenger-dependence and concentration-dependence tests. Certainly the use of the two together is far superior to reliance on either one alone. The reaction mechanism would have to be perverse or grossly simple to produce a product which passes both tests but is not a cage product. An example of the latter would be a reaction which gives only a single product; in such a case, isotopic labeling could be used to separate cage processes

from non-cage processes.

Establishing a cage mechanism for formation of the butadiene 13 is more difficult because it does not seem to be very stable under the reaction conditions; addition of a radical to the terminal methylene group to give a highly stabilized phenylallyl radical apparently competes with attack on the bulk solvent. In the concentration study of Table 4, the observed yield of the diene is substantially higher for the lower initial perester concentrations. This can be attributed to diversion of attack of radicals from a diene to solvent as the ratio of solvent to diene is increased.

The higher yields of the diene at the higher 1,4-cyclohexadiene concentrations in Table 1 apparently reflect the fact that primary reaction products can also be protected by making the solvent more reactive. It seems significant that for decomposition of 1 in the relatively inert solvents cyclohexane, ether, and tetrahydrofuran (see Table 8) no diene is detected. The yield of the ether 12 also varies to some degree, but not so dramatically (see below).

Perhaps the best argument that the diene is a cage product is that other mechanistic possibilities predict that the yield of diene should decrease strongly on going to lower initial perester concentrations. For example, this is definitely the prediction for disproportionation of the ring-opened radical 3 with any species subsequent to diffusion from the solvent cage. The reason is that the ring-opened radicals have other options (e.g., ring-cyclization to the radical 9 or abstraction of hydrogen from solvent) and thus will be unable to wait out the longer time required for another radical species to make an appearance.

Taking the run in Table 4 at 0.001 M initial perester concentration as most likely to offer the best protection to once-formed diene and ether, our best guess for the disproportionation to combination ratio for a t-butoxy radical and a diphenylbutenyl radical under these cage-reaction conditions is 2.1/18 = 0.12.

Variation of the yield of the ether 12 with solvent composition might arise from radical-induced decomposition in some of the solvents, from subsequent radical attack on the ether, or might simply reflect physical differences among the various solvents in their ability to keep the caged particles long confined. If the latter is correct, we should expect the ether yields to correlate with properties of the solvent which reflect particle mobility. The success of one such correlation is explored in the following paragraphs.

Chandrasekar (40) has employed a generalized random-walk model to express the probability that a point particle which is at a certain point at time zero will be within a volume element centered at some second point at a later time t. Consider a situation in which the centers of two particles are initially separated by a distance r_0. If we assume that the probability per unit time that two particles in such a real system undergo cage reaction at time t is proportional to the probability that centers of the particles are arbitrarily close in the point-particle model system, then the integral overall time of Chandrasekar's eq. 107 (which expresses the latter probability) should be proportional to the net probability that cage reaction will take place. This treatment predicts that the cage efficiency will be proportional to $1/r_0D$, where D is

the sum of the diffusion coefficients for the two particles.

Unfortunately, experimental data concerning diffusion coefficients are not sufficiently extensive to allow the prediction of diffusion coefficients for the two radicals of present interest. However, to judge how cage yields might vary from solvent to solvent, we need only estimate how the diffusion coefficients will vary, and for that we can employ a recent equation due to Houghton (70). The equation expresses self-diffusion coefficients (e. g., for diffusion of a cyclohexane molecule in cyclohexane solution, etc.) in terms of the quantity $T\rho/\eta$, where ρ is the density and η the viscosity of the medium in question. Unfortunately, a self-diffusion coefficient must depend on the type of molecule which is undergoing the diffusion as well as on the properties of the surrounding solvent. Thus, the relative diffusion coefficients of a third species in each of two solvents need not be very similar to the relative self-diffusion coefficients.

Still, we have little choice but to assume, if Chandrasekar's random flights treatment is applicable, that cage efficiencies will be proportional to reciprocal self-diffusion coefficients. Thus, in Fig. 5 the yield of the ring-opened ether 12 is plotted against the so-called kinematic viscosity, which is given by η/ρ, where η is in centapoise.

By this point, the reader should have accumulated a healthy respect for the approximations which have been made. In addition, in compiling the figure ether yields at 131° (where several have been measured) have had to be employed in connection with viscosities at 20° (where several are available and the others could be measured). Also, the yield of 12 in n-octane at 110° (Table 8) has been approximately cor-

rected to 131° by assuming a temperature variation similar to that observed in cyclohexane – cyclohexadiene mixtures (Table 1). Finally, the directly measured cyclohexane value (14%, Table 8) has been discarded in favor of the value of 18% obtained from Table 1 by extrapolation to zero cyclohexane concentration, since the former value may in part be determined by subsequent radical attack on the ether in neat cyclohexane.

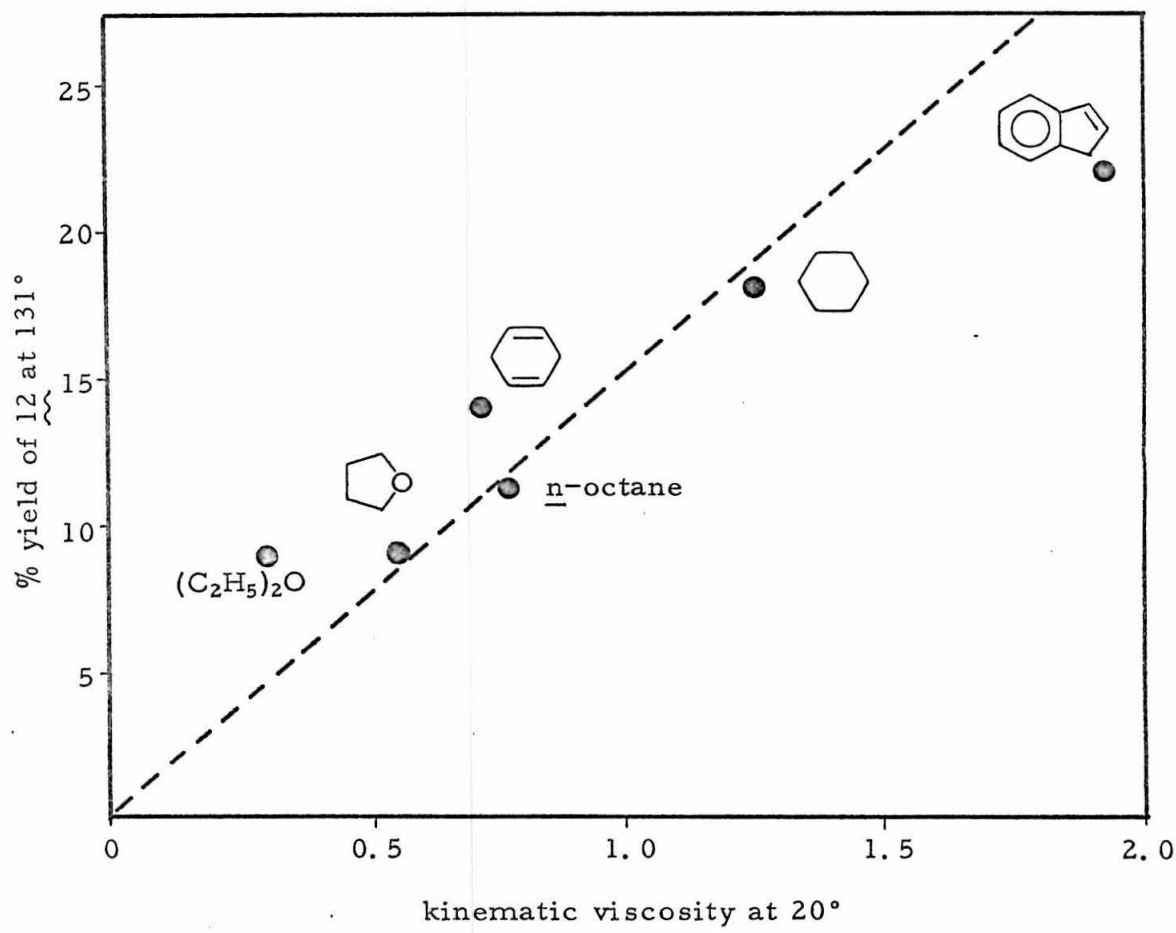


Figure 5. Variation in yield of the ether 12 with kinematic viscosity.

Although the 'theoretical' zero-intercept line does not give a fit of surpassing excellence, the trend is nevertheless roughly as expected. If anything, the points for the poorly hydrogen-donating solvents diethyl ether, tetrahydrofuran, and n-octane tend to be high. On this basis, it may be tentatively suggested that there is little or no radical-induced decomposition of the ring-opened perester 1 in any of the hydrocarbon or ether solvents studied. The low material balances for decomposition of the peresters in the poorly hydrogen-donating solvents would then be ascribed to inefficient conversion of the ring-cyclized radical 9 to the dihydronaphthalene 10.

(2.) In the Presence of Triethyltin Hydride

With yields of the ring-opened ether 12 in the ether and hydrocarbon solvents freshly in mind, the reader's attention is directed to Table 10, where yields of 12 for decomposition of 1 in solutions of triethyltin hydride in n-octane are listed (see also Fig. 4 which follows Table 10). The highest yield reported, about 4 percent, is far below the 16 to 20 observed for decomposition of 1 in the presence of 1,4-cyclohexadiene or the 13% in essentially neat n-octane. The most striking feature, however, is the major decrease in the observed yield of the ether 12 with increasing triethyltin hydride concentration.

That decrease might reasonably be due to any of three factors, or to a combination of the three: (a) a change in mechanism with radical-induced decomposition strongly predominating at the higher tin hydride concentrations; (b) formation --but subsequent destruction--of a normal

amount of cage product, with the destruction--presumably via the known process of hydrostannation (41)--becoming increasingly efficient at the higher tin hydride concentrations; or (c) interdiction of the cage processes via facile abstraction of hydrogen from tin hydride by one or both of the caged species. The correct answer is alternative (a), though we will find that some contribution by the other possibilities cannot be ruled out at the higher tin hydride concentrations.

Note the clear kinetic implications of alternative (a): if the normal process makes only a small contribution, at each stage of the reaction, several perester molecules must fall by way of induced decomposition for each that dies of old age. Thus, if (a) is correct, unusually low yields of the ether must be associated with unusually high rates of decomposition.

Kinetic evidence reported in subsection 9 confirms this idea. For example, the half-life of 1 in chlorobenzene solution at 110° is about 150 minutes (21). For 0.01 M triethyltin hydride in n-octane, the half-life at 110° of an 0.002 M solution of 1 was found to be about 53 minutes. Moreover, in the presence of 0.4 M tin hydride under otherwise identical conditions, the half-life is only about 6 minutes.

It should be apparent that both kinetic measurements and yields of the cage ether 12 convey information concerning the relative amounts of normal and induced decomposition. Extraction of that information from the ether yields is straight-forward. The one additional piece of information we require is the yield of ether 12 for decomposition of 1 in n-octane alone. At 110° a yield of 13% was found for decomposition of 0.01 M perester in n-octane (with 0.2 M cyclohexadiene added to

moderate the reaction and insure the survival of the ether (see row 5 of Table 8)). The yield of ether at higher temperatures should be similar, though somewhat smaller than at 110°, perhaps showing nearly the same temperature dependence as found for decomposition of 1 in the presence of 1,4-cyclohexadiene in cyclohexane (see Table 1). Thus, the fraction of normal decomposition for the runs in Table 10 at 125° can be estimated by dividing the observed yield of the ether by about 12.

Extraction of the same information from the kinetic measurements proceeds as follows: If the induced process is first order in perester--we will show in subsection 9 that it is for the runs of Table 10--the fraction of normal decomposition is simply given by the ratio of half-lives in the presence and in the absence of triethyltin hydride.

Thus, the compatibility of the two types of measurements can be tested. If no other factors were involved, that test would be made at this point. However, the fraction of normal decomposition can also be predicted from the stoichiometry of the reaction. This is most easily seen by noting that superposition of an induced decomposition on the normal process constitutes a chain reaction whose chain length is determined by the nature of the termination processes. Each induced decomposition consumes one triethyltin radical; if the chain is to be propagated without attenuation, the tin radical consumed must invariably be regenerated. Among the reaction products is the dihydronaphthalene 10, whose formation requires the loss of a hydrogen atom by a ring-cyclized radical 9 to some second species. Thus, if the induced decomposition ultimately results in formation of the dihydronaphthalene, the tin radical will not be regenerated. Moreover, if the loss of the hydro-

gen atom by $\underset{\sim}{9}$ occurs to a triethyltin radical, not just one, but two chains will be stopped. Incidentially, it is the predominant termination of chains in this manner which makes the induced decomposition first order in the perester concentration; chain termination by dimerization of triethyltin radicals would lead to three-halves order kinetics (39).

I should mention at this point, although it may already be clear to the reader, that relating the stoichiometry to the amounts of normal and induced decomposition presents greater difficulties than are involved in the implementation of the two other procedures. In fact, the process of obtaining agreement between the three approaches will enable us to determine more precisely than would otherwise be possible the relative rates of ring-cyclization and abstraction of hydrogen from triethyltin hydride by ring-opened radicals. These are important quantities because they are involved in elucidating the response of the radical system to the activity of the hydrogen donor.

To make best use of the stoichiometry approach, we shall need to know how the ring-cyclized radicals are consumed under less complicated circumstances, such as are found for decomposition of the peresters in the presence of 1,4-cyclohexadiene. This knowledge will help us to decide, where hypothesis is necessary, what reactions of the ring-cyclized radicals are most likely under the present circumstances. Therefore, we shall postpone the full discussion of the nature of the induced decomposition until subsection 9.

Before leaving this discussion entirely, I would like to clarify one point that was implicit in the above: triethyltin radicals attack the per-

ester with about equal facility at each of the two peroxy oxygens (see Chart 6, p. 162). This conclusion appears to be required by the following line of reasoning. Hydrocarbon products are formed to the extent of 30 to 40 percent (except at the higher tin hydride concentrations at 144°, where extensive destruction of products via their hydrostannation and that of the perester itself evidently occurs). The significant point is that these hydrocarbons are major products even in circumstances where cage-ether yields indicate that induced decomposition strongly predominates. This fact requires that there be a way to form hydrocarbon products via the induced process. Presumably, attack of triethyltin radicals on the perester often affords t-butoxytriethyltin and the acyloxy radical 11, which then decarboxylates to give the ring-opened radical 3, etc.

The products of the alternative attack by the tin radicals are a t-butoxy radical and triethyltin (γ, γ-diphenylallyl)acetate, 14. Yields of the tin ester, where measured (by infrared absorbance or by weight)

$$(C_6H_5)_2C{=}CHCH_2CH_2CO_2Sn(C_2H_5)_3$$

14

are given in Table 10. I should caution, however, that the two values quoted in the bank of runs at 125° actually were determined for closely similar perester and tin hydride concentrations at 110°; they are listed in the 125° bank to conserve space and to allow an approximate accounting of material balances in the two runs in question.

Yields of the diene 13 have not been recorded in Table 10. The

vpc traces allow, at most, yields of 0.2 percent, except for two or three cases in which appearance of a new material at slightly longer retention time would have obscured yields of up to 1 percent. Thus, quantitatively meaningful estimates of the diene yields cannot be extracted from the data. Moreover, from the disproportion to combination ratio of 0.12 estimated for the runs in 1,4-cyclohexadiene, it is clear that the diene yields here should be small. It is also probable that much of what little diene is formed is subsequently hydrostannated (41), and thus not observed.

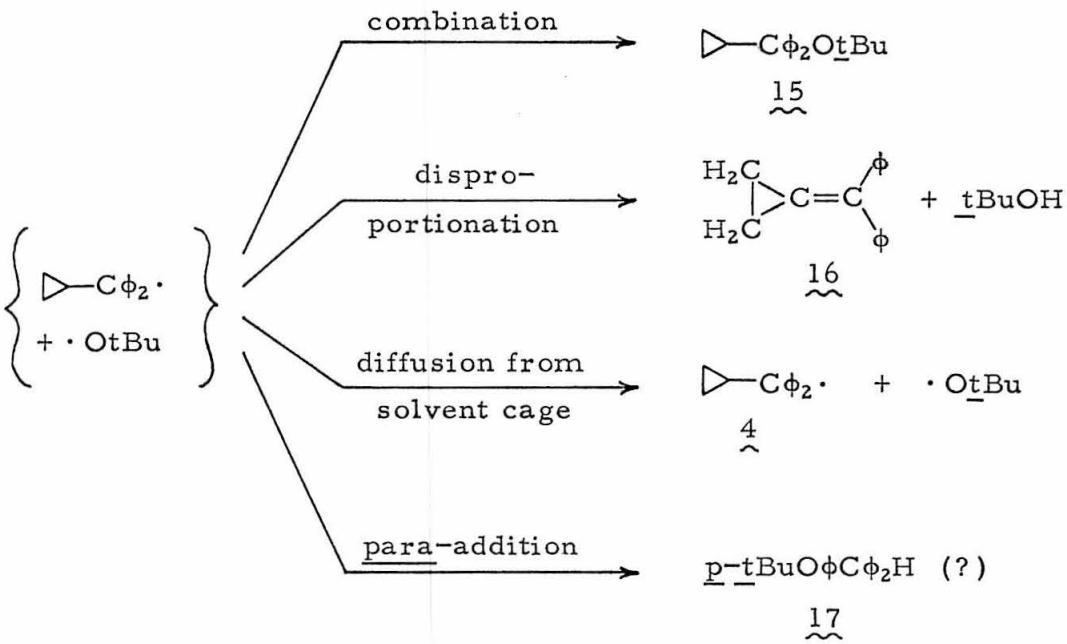
B. t-Butyl Diphenylcyclopropylperacetate

Decomposition of the ring-closed perester 2 is expected to produce, in the initial solvent cage, a ring-closed radical 4, a molecule of carbon dioxide, and a t-butoxy radical. As with the ring-opened perester, cage recombination and disproportion competes with diffusion. In this case, the products are the ring-closed ether 15 and the diphenylmethylenecyclopropane 16.

The ring-closed ether 15 and the methylenecyclopropane 16 have so closely similar retention times on Ucon polar that they are observed as a single peak. This curious* fact held up their identification for a considerable time while endeavors were directed to fitting nmr and UV

*One might have expected the greater molecular weight of 15 to lead to a retention time comparable to that observed for the ring-opened ether 12, which comes at about twice the retention time of 15 or 16. A possible explanation is that the steric congestion in 15 prevents strong interaction with the Ucon polar stationary phase.

Chart 3. Cage Reactions in the Thermal Decomposition of t-Butyl Diphenylcyclopropylperacetate.



data to a single compound. Another problem in the identification was the difficulty experienced in separating the material from other reaction products. In fact, no better than enriched samples were ever obtained, even this being possible only by choosing especially fortunate reaction conditions. Yields of the material we are discussing are listed in the data tables in the columns for substance B (see especially Tables 2 and 9 at this point).

The reader will note that the ratio of B to other products listed is relatively large for decomposition of perester 2 in cyclohexane. With this in mind, decomposition of 1 gram of perester 2 (rather than the usual 25 mg) was carried out in cyclohexane at 70°. Workup of the product mixture by elution with pentane on a Florisil column (no attempt

being made to separate products) was followed by distillation three times in a bulb-to-bulb apparatus. Analysis of the resulting material by vpc revealed the presence of a number of products in the following relative amounts (by area): B, 32%; diphenylbutene 5, 3%; diphenylcyclopropylmethane 6, 15%; 1-phenyl-3,4-dihydronaphthalene 10, 48%; and two minor products, 2%. The material was examined by nmr and a careful integration was made. A synthetic mixture with diphenylbutene, diphenylcyclopropylmethane, and the dihydronaphthalene in the same relative amounts as for the unknown was also prepared and investigated by vpc and nmr. This allowed accurate subtraction of the absorbances due to the three known components from the nmr spectrum of the reaction mixture.

The resulting residual spectrum is given (somewhat schematically) in Fig 6. Main features are the 39 units of phenyl absorbance, the 25 units comprising the 'doublet' at about 1.25 ppm, and the 8 units in a broad absorbance at about 0.3 ppm (indicative of secondary cyclopropyl protons). The 8 units remain from an original 17, only 9 of which could be attributed to the diphenylcyclopropylmethane known to be present. Of course, all the observed resonances do not necessarily correspond to the product B; some may be due to minor products which happen to be obscured in the vpc traces by some of the other products. Even so, only frustration was experienced in trying to divine a single structure which might account for even a major part of the observed resonances.

The critical clue in the resolution of the problem arose in another 'large-scale' run, this time in neat 1,4-cyclohexadiene. A nmr spec-

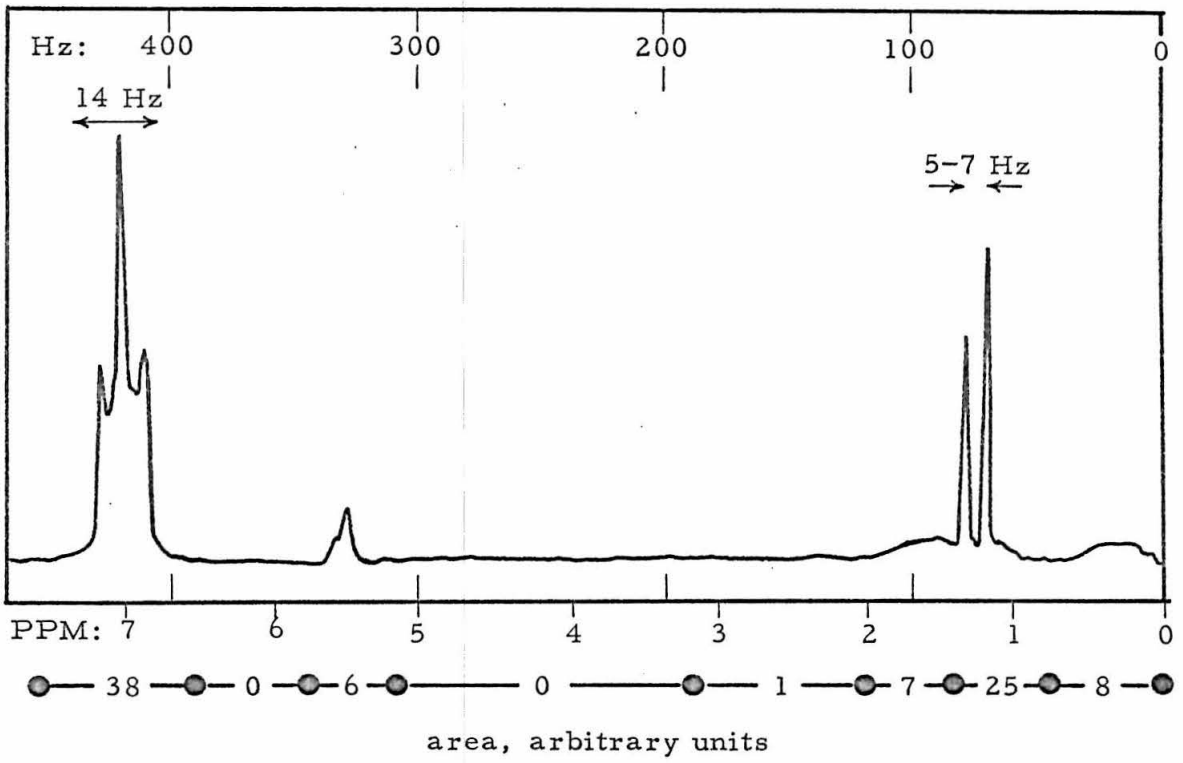


Figure 6. Residual nmr spectrum showing absorbance due to B

trum obtained on a distilled (but not chromatographed) sample again showed the upfield doublet, but the ratio of upfield to downfield peaks was about 6:1 rather than the 3:2 previously observed for decomposition in cyclohexane. Moreover, after careful chromatography on acid-washed alumina, the upfield peak disappeared entirely, though the down-field peak was apparently unaffected. Clearly, the components of the doublet are due to at least two substances. This inference allows an interpretation of Fig. 6. The 10 unit down-field peak is due to the methylenecyclopropane. The associated phenyl absorbance is 25 units. Thus the 15 unit upfield peak goes with about 13 units of phenyl absorb-

ance, the 8 units of cyclopropyl-region absorbance, and possibly with some of the other absorbancies. The ring-closed ether 15 has 10 phenyl protons, 9 methyl protons, 4 secondary cyclopropyl protons, and one tertiary cyclopropyl proton. In view of the errors expected to be accumulated in obtaining the difference spectrum, the 10:9:4 agrees quite reasonably with the 13:15:8 inferred from Fig. 6.

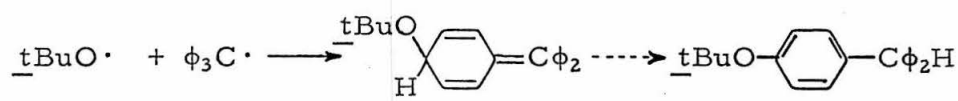
An independently prepared sample of the methylenecyclopropane was found to have the expected retention time on Ucon polar. Addition of a quantity of 16 to a reaction mixture containing a like amount of the candidate material was found to double the height of the 1.3 ppm singlet without detectably broadening it. This information would seem to establish the methylenecyclopropane as a reaction product.

The knowledge that it is also a cage product is due to a curious quirk of fate. The column used to obtain initial vpc traces for the concentration-study runs of Table 6 unexpectedly separated the product B into two peaks, one of which displayed the same retention time as the methylenecyclopropane on that column. That vpc column was prepared from a sample of Ucon polar carrying the same markings (50 HB 5100) as Ucon polar previously employed. However, a column made up from yet another sample of Ucon polar 50 HB 5100 caused the two peaks to again coalesce. Table 6 shows that the yield of the methylenecyclopropane varied little with the initial perester concentration. Because we know that the ring-cyclized radicals (from which the methylenecyclopropane must somehow be formed) have other options, the constancy of the yield indicates a cage-disproportionation origin.

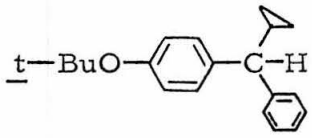
Similarities to Lorand and Bartlett's study of t-butyl triphenyl-

peracetate (27) must be noted here. Lorand and Bartlett found evidence that t-butyl triphenylmethyl ether is formed. As in this work, they were not able to isolate the ether, although nmr spectra of samples of the crude reaction mixture showed a peak at high field attributable to t-butyl protons. Upon chromatography on alumina, they obtained triphenylcarbinol, whose formation they attributed to cleavage of the ether on the column in view of the fact that infrared spectra showed that the carbinol was not present in the crude reaction mixture. Similarly, in this work the diphenylcyclopropylcarbinol was isolated in about the expected amount via careful chromatography on Florisil of the products of another 'large-scale' run. Finally, Lorand and Bartlett point out that t-butoxy triphenylmethyl ether is unknown; several attempts to prepare the ring-closed ether 15 in this work were uniformly unsuccessful.

Triphenylmethyl radicals, Lorand and Bartlett found, tend to do rather desperate things: evidently the space around the central carbon of the triphenylmethyl radical is so congested that the caged t-butoxy radical finds it about equally easy to attack a phenyl ring at the para-position to give a quinoid product, which is converted under the reaction conditions to p-t-butoxytriphenylmethane. The analogous product



for this work, 17, was shown by nmr to be present, if at all, in a yield of less than about 3 percent. However, an unidentified vpc peak which comes at approximately the retention time expected for the ring-opened



17

ether and whose area runs about 4-6% of that of the product B might well be due to that product. Of course, if the peak corresponded to ring-opened ether, and if the ring-opened material could be shown not to result simply from isomerization of the ring-closed ether, that result would be of interest in regard to possible formation of both ring-opened and ring-closed products from a common intermediate.

The reader will note that a product labeled B is listed in Table 1 for decomposition of the ring-opened perester. However, that material is not thought to be either the methylenecyclopropane 16 or the ring-closed ether 15. The same designation has been used because a peak is also found at the retention time of 'B' when the perester employed is 1. My feeling is that the material designated B for decomposition of perester 1 is likely to be a 1-phenyltetrahydronaphthalene (or perhaps several isomeric 1-phenyltetrahydronaphthalenes (see Chart 4)). Its probable mechanism of formation is as follows: Ring-cyclized radicals are converted, somewhat inefficiently, to the dihydronaphthalene 10 via disproportionation reactions. If pairs of ring-cyclized radicals disproportionate, one of the products will be a tetrahydronaphthalene. Moreover, disproportionation of a ring-cyclized radical with a cyclohexadienyl radical can either produce dihydronaphthalene plus 1,3- or 1,4-cyclohexadiene, or a tetrahydronaphthalene plus benzene. In partial support of this identification, we can note that the be-

Chart 4. Possible Structures for Isomeric 1-Phenyltetrahydronaphthalenes.

havior of B as a function of the initial cyclohexadiene concentration in Table 1 is similar to that of the dihydronaphthalene 10. Further evidence will be considered later (pp. 129, 130, 281, 282).

If tetrahydronaphthalene is formed in the decomposition of the ring-opened perester, it should also be formed from the ring-closed perester. In fact, the product labeled B_1 in the Table 6 concentration study is likely to be tetrahydronaphthalene. Indeed, the unexplained absorbances in Fig. 6 could well be due to such a product(s). If this is correct, then what has happened to the ring-closed ether? We have already alluded to the instability of the ether on (acid-washed) alumina and to unsuccessful attempts to synthesize the ether. It is easy to imagine that acid-catalyzed cleavage might be a facile process. The perester 2 is prepared by the method of Lorand and Bartlett (27) from the acid chloride and sodium t-butylhydroperoxide; if the heterogeneous reaction is not carried to completion and the work up (by recrystallization from pentane at low temperature) does not eliminate all the acid chloride, the contaminated perester may develop HCl on decomposition.

Thus, the ring-closed ether might reasonably be observed or not depending on the purity of the perester. Examination of the yields of B suggests that the ether wholly or largely survived the reaction conditions for the runs of Table 2, for some of the runs of Table 9, and, fortunately, for the 'large-scale' decompositions referred to above; but not for the runs of Table 6, Table 7, or for other runs in Table 9.

If this interpretation is correct, we can use the results of Table 6 to divide as follows the 36% B reported in Table 2 for 2 in 2.8 M 1,4-cyclohexadiene at 35°: 7% is diphenylmethylenecyclopropane, a like amount is tetrahydronaphthalene, and the remainder, 21%, is ring-closed ether. Thus, the total amount of cage product is about 28% and the disporportionation to combination ratio is estimated to be about 7/21 = 0.33. Interestingly, the 6:1 nmr intensity ratio previously remarked for the large scale decomposition in 1,4-cyclohexadiene gives an estimate of 1/4:6/9 = 0.38, in rather decent agreement with the value inferred by vpc.

The reader will recall that for the ring-opened radical and the t-butoxy radical the disproportionation to combination ratio is about 0.12 (page 63). Considering that the ring-opened radical has two disproportionable hydrogens to one for the ring-closed radical and that the double bond in the methylenecyclopropane must be highly strained (71), that the disproportionation to combination ratio is substantially higher when the ring-closed radical is involved seems surprising. Perhaps the congestion about the radical center in the ring-closed radical is responsible for selectively disadvantaging its participation in combination reactions; the hydrogen atom removed by the t-butoxy radical in

disproportionation is located a few angstroms from the center of greatest steric congestion.

Yet we note that as much or possibly even greater amounts of cage product are formed in decomposition of the ring-closed perester 2. If the rate constant for combination of a ring-closed radical with a t-butoxy radical is appreciably less than that for combination of the ring-opened radical with the t-butoxy radical, why are the cage efficiencies in the inverse order? The lower decomposition temperatures for the ring-closed perester may be part of the answer, although the small temperature dependence of the cage processes for the ring-opened perester (see Table 1) suggests that this factor should not be large. The attractive explanation, it seems to me, is that most or all of the ring-opened perester decomposes by the stepwise pathway (see p. 51); the time necessary for decarboxylation of the acyloxy radical 11, of course, decreases the potential cage efficiency. In contrast, decomposition of the ring-closed perester is expected to be concerted and the warring partners can have at it from the start.

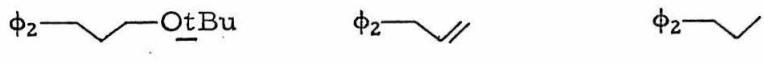
With the preliminary discussion of induced decomposition of the ring-opened perester in triethyltin hydride freshly in mind, we might ask whether induced decomposition can be inferred for the ring-closed perester as well (Table 11). Unfortunately, another product at nearly the same retention time as B is formed in those decompositions. Judging from peak areas found for some runs and from the high material balances quoted in Table 11, the new product does not contain the C_{16} fragment from the perester. That product might possibly be hexaethyl-

ditin. At any rate, the new material generally obscures the retention time region where the cage-products would be found.

Thus, while it is possible that induced decomposition occurs for the ring-closed perester, kinetic measurements would be needed to be sure. We can, however, say that, if induced decomposition is important, it must give principally t-butoxytriethyltin and the ring-closed acyloxy radical. For the ring-opened perester, as noted above (p. 70), triethyltin radicals attack either of the peroxy oxygens with comparable facility. Of course, the necessity to propose a different pattern for the ring-closed perester cannot be used as an argument against induced decomposition for 2, for the steric congestion associated with the phenyl rings might well account for just such a shift in the position of attack.

C. t-Butyl 4,4-Diphenylperpentanoate

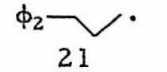
Yields of the saturated ether 18 (Table 3) are remarkably similar to those for the ring-opened ether 12 (Table 1). As we shall document later on, the ring-closed radical strongly predominates in its equilibrium with the ring-opened radical at all temperatures studied. Thus, the similarity between yields of the ethers 12 and 18 strongly suggests that the isomerization of ring-opened radical to ring-closed radical does not take place on nearly as short a time scale as do the cage processes. Although the time scale for cage processes (24) is uncertain, this consideration would appear to set a maximum of about 10^8 to 10^9 for the rate constant describing the isomerization of ring-opened 3 to ring-closed 4.



18 19 20

A product believed to be 1, 1-diphenyl-3-butene (19) is found at slightly longer retention time than the saturated hydrocarbon 20. For decomposition in cyclohexane, its yield could be determined to be 2. 0%. However, the massive yields of 20 formed in the presence of 1, 4-cyclohexadiene made it impossible to independently observe the smaller peak. Therefore, I have assumed the figure of 2. 0% is also correct in the other cases and have so corrected the total area for the two peaks in calculating yields for 20. The assumption that the mono-olefin 19 largely survives the reaction conditions in cyclohexane, whereas its unsaturated analog 13 does not, is not unreasonable in view of observations of Szwarc and co-workers (25) which show that methyl radicals add to butadiene or to 1, 1-diphenylethylene about 50 times more rapidly than to ethylene.

Thus, the disproportionation to combination ratio for the saturated radical 21 and the t-butoxy radical may be taken to be greater than or equal to 2. 0/20 = 0. 1. That this quantity is nearly the same as for the unsaturated ring-opened radical with t-butoxy (0. 12) implies that formation of the conjugated pi-electron system of the butadiene 13 does not greatly facilitate disproportionation. Such a result seems appropriate for a diffusion-controlled process, which, by virtue of successful competition with diffusion from the solvent cage, each cage reaction is.



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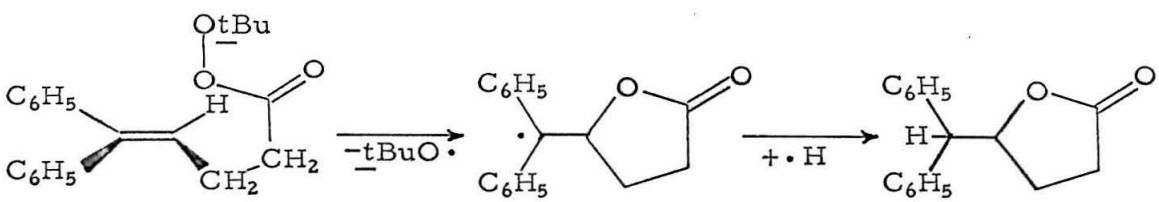
The regular decline in the yields of 18 as 1,4-cyclohexadiene replaces cyclohexane as solvent would appear to be a good example of the previously discussed dependence of cage yields on solvent viscosity.

6. Molecule-Induced Decomposition of t-Butyl (γ,γ-Diphenylallyl)peracetate

Of the three perester-decomposition mechanisms briefly surveyed in subsection 3, we have now covered normal homolytic decomposition and have made a start on radical-induced decomposition in triethyltin hydride. The third, molecule-induced decomposition, is possible in the ring-opened perester 1 because of the presence of the carbon-carbon double bond, but in the ring-closed perester 2 and the saturated perester 8 the necessary functionality is lacking. As stated in subsection 3, the essence of molecule-induced decomposition in 1 or in the closely related ortho-diphenylvinylperbenzoate system studied by Martin and co-workers (29) is attack of the double bond on the peroxy linkage to give a cyclic lactonyl radical and a t-butoxy radical. By analogy with Martin's system, the lactonyl radical may in part undergo



1 22 23

cage combination with the t-butoxy radical, but the dominant reaction is expected to be the one shown, hydrogen abstraction to give the lactone

23. Loss of a hydrogen atom by 22 to give the exocyclic unsaturated lactone may also occur.

Actually, the evidence for molecule-induced decomposition of 1 is only circumstantial in that no product arising via that mechanism (such as the lactone 23) has actually been isolated and subjected to analytical scrutiny. In truth, efforts to that end were begun only very late in the course of this research, and it was just not possible to spare sufficient time to carry through to that point. As circumstantial evidence goes, however, the evidence is rather good. Because the existence of molecule-induced decomposition affects the product ratios described in the quantitative mechanistic study of Section Two, it seems worthwhile to bring up the subject at this point.

The first significant observation is that a long retention-time product can be detected by vpc among the reaction products from the ring-opened perester 1 but not from the ring-closed 2. For short, let us call this material product X. The retention time of X is about 10 times that of the ring-opened t-butyl ether 12 on Ucon polar and 3 times that of 12 on silicone oil. These observations suggest (a) that X is not dimeric material formed from solvent radicals or hydrocarbon radicals derived from the peresters, since such a product should be formed both from 1 and 2, and (b) that the material is appreciably polar (this would nicely explain the difference in relative retention times of X and 12 on silicone oil and the more polar Ucon polar).

Yields of X for decomposition of 1 are shown in Table 1 as yields of the lactone 23 (which is what we shall conclude X is). There is no clear trend of yield with 1,4-cyclohexadiene concentration or with

reaction temperature. The average yield is about 15%. The product was also detected in the concentration study reported in Table 4. Those observations have not been dignified by inclusion in Table 4, however, because the resolution on the particular silicone oil column employed allowed only semiquantitative accuracy. Nonetheless, a definitive result was obtained in the finding that X does not decrease in yield on going to lower initial perester concentration (the yield may actually increase by about a fourth). This clearly means that X cannot be a radical-induced product (such as a cyclohexadienyl ester of the ring-opened acid).

The possibilities excluded by the information presented above and the analogy to the benzoate system already combine to suggest that X is the lactone 23. Martin has reported that the rates of molecule-induced decomposition in his systems respond strongly to solvent polarity. For example, Martin's diphenylvinylperbenzoate decomposed 62 times as rapidly in methanol as in chlorobenzene (29a). With this in mind, decomposition of a sample of 1 of 10% 1,4-cyclohexadiene in methanol (v/v) was effected by maintaining the degassed reaction mixture at 100° for 100 hours (which is about 10 half-lives at the normal decomposition rate). First analyzed were the yields of the normal decomposition products (row 8 of Table 8). As expected, those yields are uniformly down by about a factor of 10. Were the yield of X also up from 15 to about 90%, the solvent change would be judged to have promoted the rate of the molecule-induced decomposition by about the factor of 60 expected by analogy to Martin's benzoate system.

This simple result, however, was not to be. Detected among

the reaction products were the ring-opened acid (15%) and the methyl ester of the acid (also 25%) as well as X (still 15%). The acid was isolated by extraction with sodium bicarbonate and identified by its melting point and its infrared spectrum (carbonyl maximum 1710 cm^{-1}). The methyl ester was identified by its vpc retention time on silicone oil, by the presence of characteristic peaks in several nmr spectra, and by the position and intensity of its carbonyl maximum at 1740 cm^{-1}. The product X from this run had the same retention time on silicone oil as did that from a run in 1,4-cyclohexadiene analyzed at the same time. The formation of the methyl ester of the ring-opened acid can be attributed to direct methanolysis of the perester.* As regards the ring-opened acid, however, well, there could well have been stoichiometrically-sufficient water to account for its formation, but my understanding is that methanol is generally more nucleophilic than water; thus, on a kinetic basis, the formation of comparable amounts of the acid and the methyl ester is hard to rationalize. That only a 4% yield of the acid could be detected in the companion run in 1,4-cyclohexadiene

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*Methanolysis of an anhydride would be expected to be rapid, while methanolysis of an ester would probably not be observed under the conditions employed. As the pK_a of t-butylhydroperoxide (12.8 (74)) lies between those of organic acids (about 5) and alcohols (about 17), methanolysis of 1 is perhaps not too surprising. A sample of the saturated perester 8 was treated similarly as regards solvent composition and reaction temperature. Again, the normal decomposition products were down in yield by approximately a factor of 10, and presumably methanolysis has occurred here also. A product at about the same retention time as the methyl ester of the ring-opened acid was detected by vpc and carbonyl bands at 1715 and 1745 cm^{-1} (appropriate for the saturated acid and its methyl ester, respectively) were observed in very nearly the same relative intensity as for methanolysis of 1.

mentioned just above makes a free-radical mechanism highly improbable as the source of a 25% yield of the acid.

One possible difficulty in Martin's interpretation of his results (29a) should be mentioned here. The enhanced rate of decomposition in methanol was ascertained (a) by following the consumption of the perester by UV spectroscopy and (b) by following by UV the decolorization of an excess of the colored free-radical scavenger galvinoxyl (75). However, no product studies were cited for decomposition in methanol. The authors mention that the rate constant from the galvinoxyl decolorization is only semiquantitative because galvinoxyl slowly reacts with methanol at the temperature employed (90°). As t-butyl hydroperoxide, the expected by product of methanolysis, is an oxidizing agent and is substantially more acidic than methanol, it is at least possible that decolorization of galvinoxyl would also accompany methanolysis. Thus, whether the 62-fold rate enhancement in methanol is due entirely to the increased rate of molecule-induced decomposition must be regarded as uncertain.

After extraction with sodium bicarbonate, then, the reaction mixture contained a small amount of hydrocarbon products, the product X, the methyl ester, and possibly other products accounting for the difference between the material balance of about 75% computed from the yields quoted above and the theoretical 100%. A partial separation of the components was simply effected by repeatedly treating the residual oil obtained by stripping the solvent with small quantities of pentane. The hydrocarbon products dissolved first, followed by the methyl ester, and, more slowly yet, the product X. The process was stopped when

the weight of the residue had been cut by four-fifths. The residue was then distilled in a small sublimation apparatus. The last few pentane extracts were then combined and similarly distilled. Obtained in this way were Fractions 1 and 2, respectively. The crude reaction mixture less the ring-opened acid (which we shall call Fraction 0) had previously been analyzed by vpc, nmr, and infrared spectroscopy, and Fractions 1 and 2 were now so analyzed. The combined data allow a test to be made of the supposition that the product X is the lactone 23.

Specifically, the ratio of X to methyl ester could be inferred for each of the fractions by each of the three methods. If for each fraction the three methods give compatible results, then the structural features on which the nmr and infrared analyses are based may safely be attributed to the product X.

The nmr ratio was obtained from relative areas of a doublet (coupling constant about 7 Hz) at 4.2 δ attributable to the tertiary dibenzylic proton of 23 and the singlet methoxyl resonance at 3.8 δ due to the methyl protons of the methyl ester. For comparison, the dibenzylic protons of diphenylmethane were found 4 Hz upfield from the center of the doublet.

The infrared ratio was taken from the absorbancies of the carbonyl maxima at 1740 cm^{-1} (the methyl ester) and 1785 cm^{-1} (X). Bellamy (88) lists 1760-1780 cm^{-1} as the range expected for the carbonyl band of a saturated γ-lactone such as 23. The ratios determined by infrared depend on the molar absorptivities assigned to the methyl ester and to X. These need not be the same; to effect something of a best fit, it has been assumed that the molar absorptivity of

X is 1.8 times that of the methyl ester.

Finally, vpc ratios were calculated assuming that X and the methyl ester have identical response characteristics.

The ratios obtained as above for the three cases are quoted in Table 14. Note that although the ratio varies significantly from sample to sample, the three analytical methods nonetheless give substantially the same results. This would seem to establish that (a) the product X

Table 14. Ratios of X to Methyl (γ, γ-diphenylallyl)acetate According to VPC, NMR, and Infrared Spectroscopy

	Ratio		
Fraction[a]	VPC	NMR	IR
0	0.62	0.6	0.59
1	4.4	4.1	5.3
2	0.29	0.28	0.24

[a]See text for origin of the various fractions.

is a carbonyl compound whose carbonyl frequency is approximately correct for a γ-lactone, and (b) the product X contains a single proton, split by only one other, which resonates at 4.2 δ, approximately the position expected for a dibenzylic proton. In addition, we also know that X is not a radical-induced product, is not acidic, is formed in the decomposition of the ring-opened perester 1 but not in that of the ring-closed perester 2, is appreciably polar and has an appreciable vapor pressure at 105° (the bath temperature employed in the vacuum distilla-

tions of Fractions 1 and 2). All of these properties admirably fit the lactone 23. In addition, evident in the nmr spectrum of Fraction 1 are absorbancies attributable to the phenyl protons, the four methylene protons, and the other tertiary proton of the lactone 23. I do not wish to leave the impression that sufficient definition was obtained in this low-concentration spectrum to attest to the correctness of the relative intensities of the various absorbancies, but at least it can be stated that absorbancies are present at the expected resonance positions.

Short of an analysis of an isolated sample, this, I feel, is pretty good evidence that X is the lactone 23.

7. Equilibration of Radicals and Hydrogen Abstraction

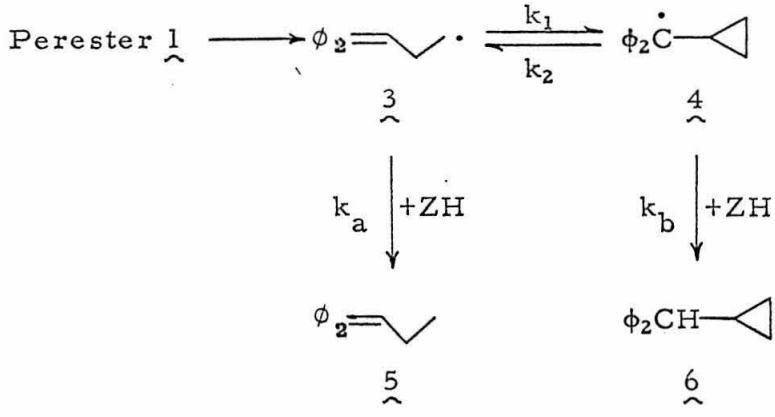
We have seen that decomposition of each of the peresters can get under way via one or more initial steps. Of particular interest is what happens next for normal or radical-induced decomposition, the pathways leading to formation of the hydrocarbon products with which we are chiefly concerned.

In the usually dominant normal decomposition, the immediate reaction products, if cage combination or disproportionation is avoided, are the t-butoxy radical and a hydrocarbon radical. For the t-butoxy radical, hydrogen abstraction should follow quickly if 1,4-cyclohexadiene, indene, or triethyltin hydride are present. In the other solvents, β-scission to a methyl radical and acetone can be competitive with or even dominate any hydrogen abstraction from solvent, especially at the higher temperatures (42). If β-scission occurs, then the resultant

methyl radical may attack the solvent; ring-cyclized radicals or solvent radicals; or products produced earlier in the decomposition, such as the isomeric hydrocarbons 5 and 6, the dihydronaphthalene 10, the butadiene 13 or, perhaps most likely, the phenyltetrahydronaphthalene(s).

No real attempt has been made to follow further the fate of the t-butoxy radical; its reactions have been so exhaustively investigated (42,43) that further study here would not likely be of great value. Actually, the question of the fate of the t-butoxy radical is of real concern in this work only for decomposition of the peresters in the presence of 1,4-cyclohexadiene and triethyltin hydride, where suppression of product destructions by the active hydrogen donors makes quantitative mechanistic treatments feasible. In these two cases, we shall simply assume that one solvent radical is formed per t-butoxy radical.

For the hydrocarbon radical, equilibration of the ring-opened and ring-closed forms is the next order of business. The nature of the cage products indicates that , at the time the t-butoxy radical takes its leave, the hydrocarbon radical nearly always will be ring-opened if the perester is ring-opened, or ring-closed if the perester is ring-closed. The radical equilibration may, of course, occur competitively with abstraction of hydrogen from the solvent. Such a situation is represented below starting from the ring-opened perester



We wish to work out an expression for the ratio of the isomeric hydrocarbons as a function of the rate constants and the concentration of the active hydrogen donor, ZH. We can proceed by writing

$$\frac{d(\underset{\sim}{5})}{d(\underset{\sim}{6})} = \frac{k_a(\underset{\sim}{3})}{k_b(\underset{\sim}{4})} .$$

Thus, we see that an expression for the ratio $\underset{\sim}{3}:\underset{\sim}{4}$ is needed. This can be obtained from the rate law for $(\underset{\sim}{4})$,

$$\frac{d(\underset{\sim}{4})}{dt} = k_1(\underset{\sim}{3}) - (k_2 + k_b(ZH))(\underset{\sim}{4}),$$

by making the steady-state approximation, $d(\underset{\sim}{4})/dt = 0$. Thus,

$$\frac{(\underset{\sim}{3})}{(\underset{\sim}{4})} = \frac{k_2 + k_b(ZH)}{k_1}$$

and

$$\frac{d(\underset{\sim}{5})}{d(\underset{\sim}{6})} = \frac{k_a k_2}{k_1 k_b} + \frac{k_a}{k_1}(ZH). \qquad (1.7\text{-}1)$$

Eq. 1.7-1 can be integrated, if the concentration of ZH does not vary appreciably over the course of the reaction, simply by replacing (ZH) by its average value as determined from the reaction stoichiometry and initial concentrations.

$$\frac{(\underset{\frown}{5})}{(\underset{\frown}{6})} = \frac{k_a k_2}{k_1 k_b} + \frac{k_a}{k_1}(ZH)_{av} \qquad (1.7\text{-}2)$$

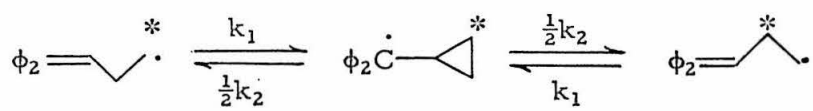
According to eq. 1.7-2, competition between radical equilibration and hydrogen abstraction should result in a linear dependence of the ratio $\underset{\frown}{5}:\underset{\frown}{6}$ on the hydrogen-donor concentration. As noted in the Overview (p. 10), Howden found no such dependence for decomposition of $\underset{\frown}{1}$ in the presence of tri-n-butyltin hydride (Howden's observations are reproduced here in Table 12). More extensive studies in this work employing instead triethyltin hydride (to simplify analysis by vpc through the use of the lower molecular-weight solvent) corroborate Howden's findings. In fact, the ratios $\underset{\frown}{5}:\underset{\frown}{6}$ given in Table 10 do not become larger at higher triethyltin hydride concentrations, but actually decrease. A similar decrease can be seen in the runs carried out by Howden at 110° (see Table 12). The reason for this behavior, which is quite unexpected, is uncertain. However, one might ascribe the trend to increasingly extensive hydrostannation (41) of the ring-opened hydrocarbon $\underset{\frown}{5}$ at the higher tin hydride concentrations.

Whatever the reason, it seems unlikely that hydrogen abstraction competes with the radical equilibration for either of the tin hydrides at the relatively high temperatures employed. Of course, a marginal degree of competition could well be obscured by whatever is respons-

ible for the observed trend.

An alternative interpretation to rapid radical equilibration would be that both hydrocarbons are formed from a common intermediate, such as the nonclassical radical 7. Because the nature of the cage products depends on the structure of the starting perester, it is obvious that a nonclassical radical cannot be formed directly from both peresters 1 and 2. Lack of dependence of product ratios on the tin hydride concentration--other than via product destructions, that is--would require that isomerization of the ring-opened radical 3 to the nonclassical radical 7 be fast compared to hydrogen abstraction by 3.

One possibility is that the nonclassical radical is much more stable than either of the classical radicals and abstracts hydrogen more rapidly than it is reconverted to either. Such an eventuality could be detected in the following way. Because the two nonequivalent methylene groups of the ring-opened radical 3 become equivalent in the ring-closed form 4,



3-α labeled labeled 4 3-β labeled

equilibration of the classical radicals must exchange the methylene groups. If isotopic labeling is used, the label will therefore be scrambled in the resultant products. On the other hand, because the methylene groups in the nonclassical radical 7 are nonequivalent, intervention of such a species provides a way of obtaining ring-closed hydrocarbon from ring-opened perester without making the methylene groups equi-

valent. If, therefore, the nonclassical radical 7 is formed irreversibly, the isotopic label would not be scrambled.

On the basis of these considerations, perester 1 was prepared with 1.4_2 g-atoms of deuterium in the α position. Following decomposition in cyclohexane at 125°, the distribution of the deuterium label in the ring-cyclized hydrocarbon 10, which is by far the major product (see for example row 1, Table 8), was determined by nmr spectroscopy. The results are summarized in Fig. 7a.

It is clear that scrambling of the deuterium label in the radical intermediates is rapid with respect to isomerization of the ring-opened radical 3 (or its equivalent) to the ring-cyclized radical 9. Here, the time during which exchange of the label may take place is limited only by the relatively slow rate at which the ortho-ring cyclization occurs.

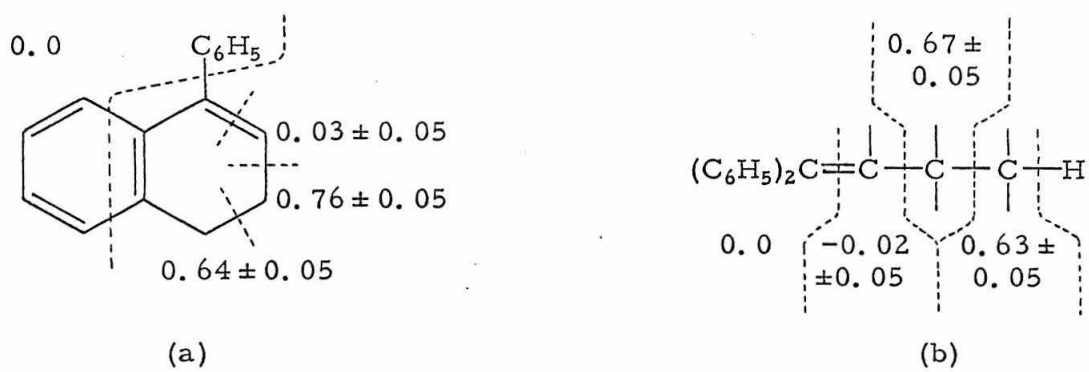


Figure 7. Distribution of the deuterium label as inferred by nmr spectroscopy in products from the decomposition of deuterium-labeled t-butyl (γ,γ-diphenylallyl)peracetate in (a) cyclohexane at 125°, and (b) 1.34 M triethyltin hydride in n-octane at 125°.

Decomposition of the labeled 1 in the presence of 1.34 M triethyltin hydride made it possible to reduce this time by approximately a factor of 8, according to the value of k_a/k_r quoted on page 135. Nonetheless, nmr analysis of the major product, the ring-opened hydrocarbon 3, showed that the processes exchanging the methylene groups are fast with respect to hydrogen abstraction from triethyltin hydride. A quantitative determination of the completeness of the exchange would require an evaluation of the secondary deuterium isotope effects which come with the method of labeling used. Indeed, if substitution of deuterium for hydrogen might be thought to constitute a major perturbation--if equilibration might correspond to a ratio of α- to β-deuterium substantially different from unity--considerable caution would have to be exercised in interpreting the data. However, the few secondary deuterium isotope effects which seem to have been reported are small, perhaps 10-15% per α-deuterium atom being a representative number at 125° (55).* In addition, the magnitude of the error limits indicated in the figure would render of doubtful value any attempt at a detailed analysis.

Thus, let us simply record that the equilibration is largely or wholly complete. This result is the first real test of the facility of the interconversion of ring-opened and ring-closed radicals which must be postulated to account for the ratios of the isomeric hydrocarbons in terms of classical radicals. The existence of the deuterium exchange

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*The β-deuterium effect in radical reactions is smaller still. A representative number is 2% per β-deuterium (72).

does not, however, in and of itself make untenable the suggestion of product control via a nonclassical radical. Such a species might be able to exchange its methylene groups via the ring-closed radical (which might be an intermediate or simply a transition state) while yet being responsible for formation of the hydrocarbon products.

The failure of triethyltin hydride to interdict the radical equilibration came as something of a disappointment because the only significantly more reactive hydrogen donors which seem to be known, free radicals with easily abstractable hydrogen atoms, would be unlikely to do any better. This is because their very reactivity restrict such free radicals to rather small concentrations; and the important factor, after all, is the product of the rate constant for hydrogen abstraction with the hydrogen-donor concentration. Fortunately, it turns out that decreasing the reaction temperature slows the rate constants for the radical interconversions more strongly than the hydrogen abstraction rate constants. As noted previously, lower reaction temperatures may be employed with ring-closed perester $\underset{\sim}{2}$ because extensive electron delocalization into the phenyl rings of the incipient ring-closed radical lowers the activation energy for the perester decomposition. Results are listed in Table 11 for decomposition of $\underset{\sim}{2}$ at 10 and 35°.

We need here the complement to eq. 1. 7-2 for entry to the radical system via the ring-closed perester. The new equation can be obtained from the old by noting that the roles played by the ring-opened and ring-closed radicals in the earlier derivation are simply interchanged. Thus, by interchanging $\underset{\sim}{6}$ and $\underset{\sim}{5}$, k_2 and k_1, and k_b and k_a, we obtain eq. 1. 7-3.

$$\frac{(6)}{(5)} = \frac{k_1 k_b}{k_a k_2} + \frac{k_b}{k_2}(ZH)_{av} \qquad (1.7\text{-}3)$$

Before proceeding to interpret product ratios according to eq. 1.7-3, we must briefly consider whether the large variations in the observed ratios could reasonably arise other than by the selective trapping of first-formed intermediate embodied in that equation. This examination is especially pertinent in view of the fact that something other than selective trapping does cause ratio variations for decomposition of perester 1 in triethyltin hydride. However, the factor tentatively implicated in that case--hydrostannation of the ring-opened hydrocarbon 5--can easily be seen to be unimportant for the runs at 35°; the high meterial balances (76 to 86%) are inconsistent with destruction of the ring-opened hydrocarbon on the scale required to explain the ratio variations. * Note that there need be no inconsistency in invoking hydrostannation of products from decomposition of 1 but not from 2, for the reaction temperatures are quite different in the two cases. Key processes may well have appreciable activation energies.

Another possibility--formation of the isomeric hydrocarbons in

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*Although yields are unavailable, a similar statement can be made for the runs at 10°. A quantity of 1-phenylnaphthalene, later realized not to have been recorded, was added to the solution of the perester from which aliquots were taken for the individual runs. Therefore, the 1-phenylnaphthalene provides a fixed, if unknown, point of reference; from the actual area measurements, it can be stated that the total yield of 5 + 6 + 10 varied even less than in the runs at 35°. One, of course, presumes that the total yields again were fairly high.

The assumption here that 6 will not be subject to hydrostannation is in accord with the ease of hydrostannation of olefinic materials and the corresponding lack of any indication that aromatic systems undergo hydrostannation (39).

part by hydrogen abstraction from some hydrogen donor other than triethyltin hydride--suffers from the apparent nonexistence of alternative hydrogen donors. Hydrogen abstraction from the ring-cyclized radical might occur, but the small yields of the ring-cyclized hydrocarbon 10 confirm the relative unimportance of such a pathway to the isomeric hydrocarbons.

Finally, the observed variations could arise from interpretation as ring-closed hydrocarbon of another product, uniquely formed under these reaction conditions, due to a fortuitous similarity in vpc retention times. Such an eventuality could have been ruled out by confirming a few of the ratios of 6:5 by nmr or by comparing retention times with those of the authentic materials on several vpc columns, but neither of these was done.

Plots at 10 and 35° of the ratio 6:5 against the average triethyltin hydride concentration (defined to be the initial tin hydride concentration less the initial perester concentration, since approximately two moles of tin hydride are used up per mole of perester taken) are given in Fig 8. The fit to a least-squares line is reasonable at each temperature.*

Two main features should be noted. The first is that the slope ($\equiv k_b/k_2$) at 10° is about twice that at 35°. The two values may be combined to give

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*In weighting the points in the least-squares fit, it was assumed that the standard error in each could be taken to be 3 percent of value. The resultant fit at each temperature gave an average percent relative deviation of approximately 3 percent. The standard errors calculated for the parameters are shown in Fig 8.

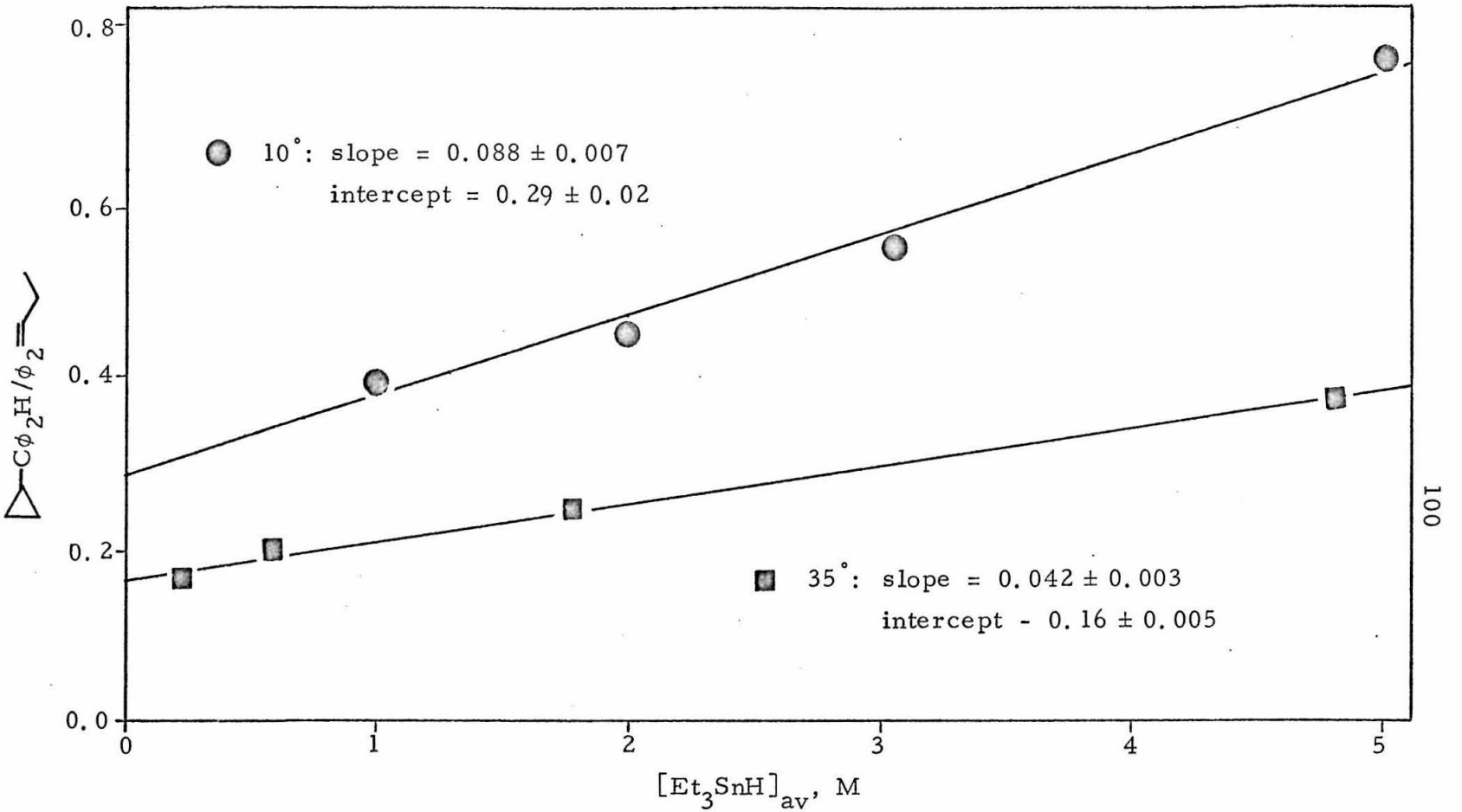

Figure 8. Variation in the ratio of ring-closed to ring-opened hydrocarbon with triethyltin hydride concentration at 10 and 35°. Error quantities are standard errors determined from the least squares fit.

$$k_b/k_2 = 2.4 \times 10^{-5} \exp(4.61/RT)^* \qquad (1.7\text{-}4)$$

Thus, we learn that the activation energy for abstraction of hydrogen by the ring-closed radical is about 5 kcal/mole less than that for isomerization to the ring-opened radical.

I must note here that the runs at 10 and 35° may not be strictly comparable because benzene was used as cosolvent for the runs at 10° whereas n-octane was employed at 35°. However, it seems unlikely that the solvent change itself is responsible for any significant variation in the trapping slopes; solvent effects in radical reactions are just not that large where electronegative atoms such as oxygen and chlorine are absent (66).

The second feature is that the intercept is also smaller at the higher temperature. If a linear extrapolation according to eq. 1.7-3 is valid, the intercept is simply the characteristic ratio mentioned in the Overview (p. 13)--the ratio of the isomeric hydrocarbons produced via hydrocarbon abstraction from a given hydrogen donor when all pertinent radical species are allowed first to equilibrate amongst themselves. As equilibration of the radical precursors of 5 and 6 is known to occur at the higher temperatures used for the decomposition of perester 1, ratios of ring-closed hydrocarbon to ring-opened hydrocarbon under those conditions should differ from intercepts observed here in a way which is consistent with a simple Arrhenius temperature dependence for the quantity k_1k_b/k_ak_2 of eq. 1.7-3.

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*A standard error of 0.73 kcal/mole in the activation energy was calculated by propagation of errors from the standard errors in the slopes indicated in Fig. 8.

Of course, in implementing this test there is the additional problen of deciding which ratios in the higher temperature experiments are most likely to be unaffected by whatever causes the variation with tin hydride concentrations remarked earlier. For lack of a better procedure, I have selected from Table 10 the two runs at about 0.01 M triethyltin hydride (by far the lowest of the tin hydride concentrations employed). The characteristic ratios of ring-closed to ring-opened hydrocarbon for those two runs and as deduced at 10 and 35° from the intercepts in Fig. 8 are plotted according to the Arrhenius equation in Fig. 9.

The four points show some scatter about the least-squares lines drawn, but on the whole the fit is adequate. Selection of other runs from Table 10 would vary the equation for the line to some degree, but would leave uneffected the obvious trend to smaller ratios of 6:5 at higher temperatures.

The equation for the least-squares line is

$$k_1 k_b / k_a k_2 = 1.5 \times 10^{-3} \exp(2.93/RT)^{*} \qquad (1.7\text{-}5)$$

Dividing eq. 1.7-4 by eq. 1.7-5 we obtain

$$k_a / k_1 = 1.6 \times 10^{-2} \exp(1.68/RT)^{**} \qquad (1.7\text{-}6)$$

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*Standard errors in the intercepts employed in the least-squares treatment were taken from Fig. 8. For the two runs at the higher temperatures, standard errors of 0.01 have been assumed. The resultant standard error in the calculated activation energy is then found to be 0.30 kcal/mole.

**The standard error in the activation energy is calculated to be 0.79 kcal/mole by propagation of errors.

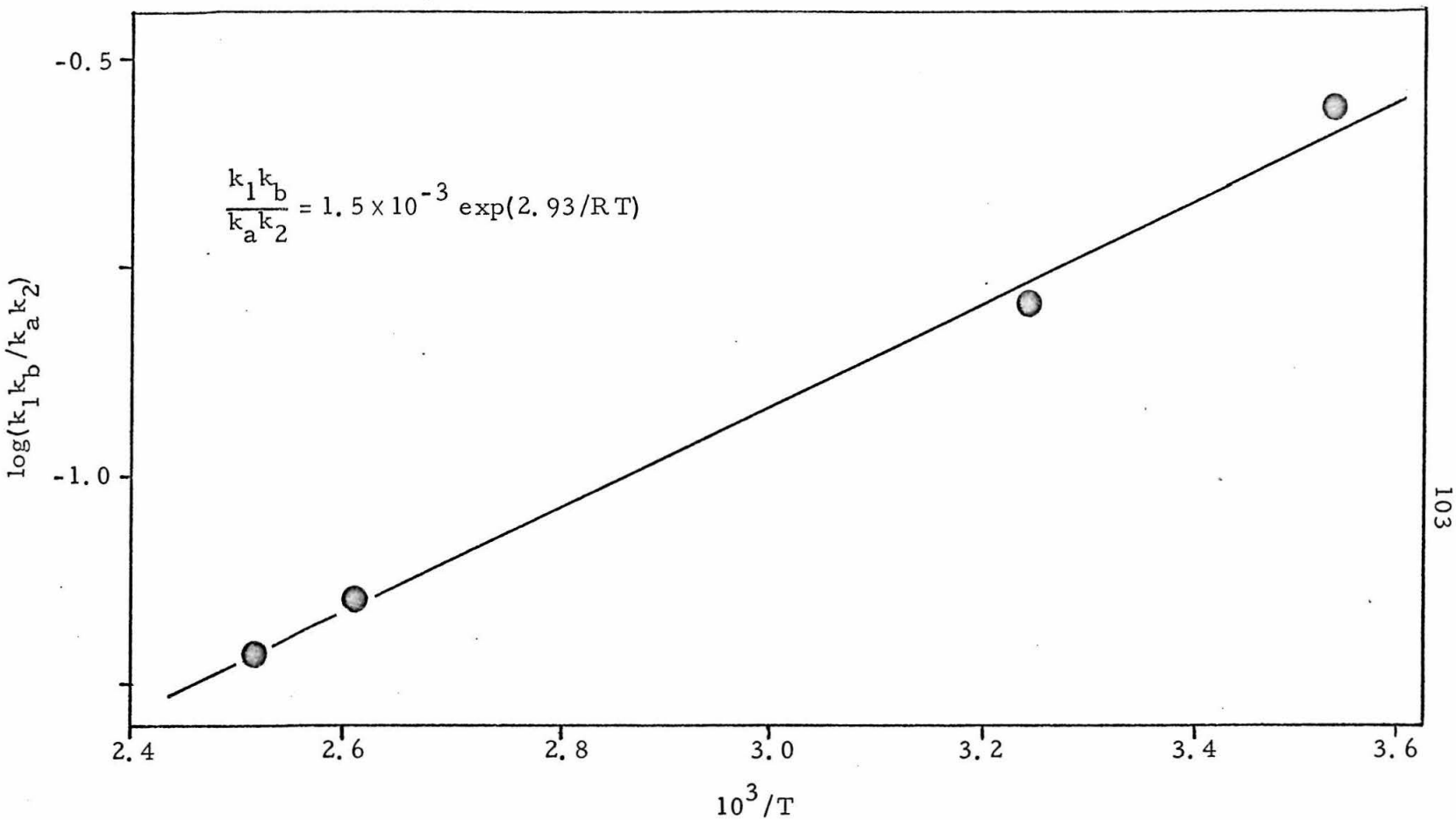


Figure 9. Arrhenius plot of characteristic ratios for hydrogen abstraction from triethyltin hydride.

The energies in the exponents of eqs. 1.7-4, -5, and -6 are related as sketched in Fig. 10. The 4.8 kcal/mole in eq. 1.7-4 is the height of the barrier for interconversion of the radicals (the center hump in Fig. 10) over that for hydrogen abstraction by the ring-closed radical (the left-most hump). Similarly, eq. 1.7-6 places the right-most barrier 2.0 kcal/mole below the radical-interconversion barrier. By subtraction, or from eq. 1.7-5, the transition state for formation of ring-closed hydrocarbon lies 4.8 - 2.0 = 2.8 kcal/mole below that for the formation of the ring-opened hydrocarbon.

The temperature dependence of the characteristic ratios thus gives us the relative positions of the two hydrogen-abstraction transition states. Placement of the transition state for interconversion of the radicals relative to the hydrogen-abstraction transition states was made possible by the measurement of product ratios under conditions where prior equilibration of the radicals does not occur. However, information derived from product ratios alone can not locate the wells for the two radicals; that requires the measurement or estimation of the activation energy for at least one reaction of each radical. Given that information, relative activation energies can be brought to bear.

The wells have been omitted in Fig. 10 to make clear what is known at this point and what is not. Later on, it will be possible not only to put in the wells, but also to include hydrogen-abstraction transition states for 1,4-cyclohexadiene and for cyclohexadienyl radicals. All but one piece of the necessary information will be developed in the present Section (i.e., Section One). Detail will gradually be added to the successors of Fig. 10 as it becomes available.

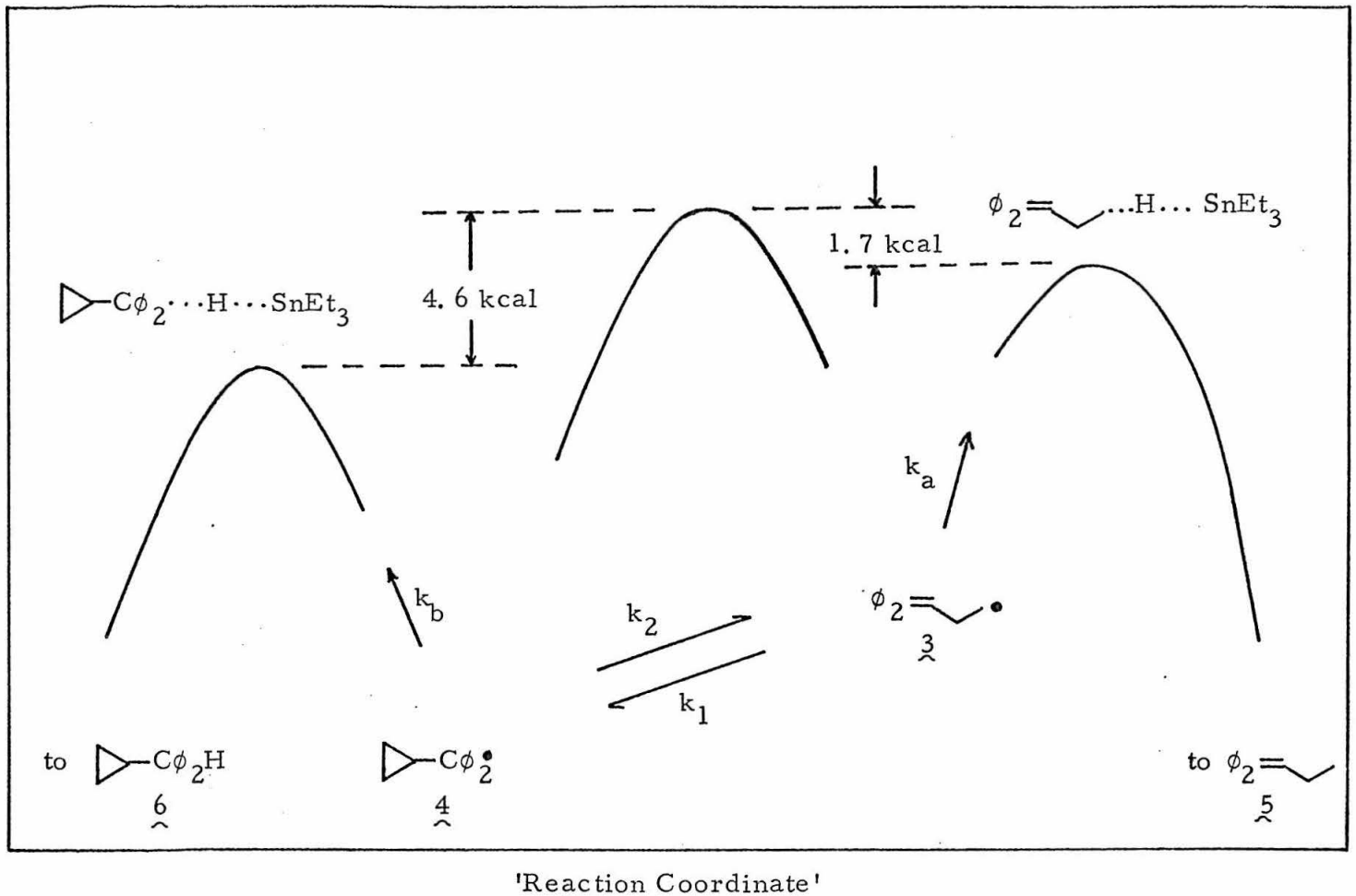


Figure 10. Relative energies of radical-interconversion and hydrogen-abstraction transition states for the ring-opened and ring-closed radicals in the presence of triethyltin hydride.

Part of Section Three will be given over to a quick review of the information by which the various levels are placed. At that time it will be possible to largely bypass embellishing arguments which must at some point be put forward, but which tend to suppress the continuity of the treatment.

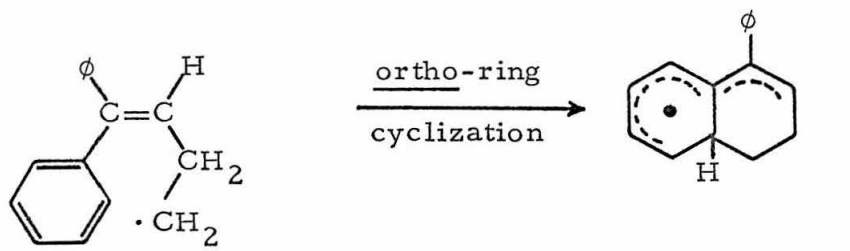
We should note, before leaving this subsection, that the present results do not rule out partial formation of both isomeric hydrocarbons from a single radical intermediate such as the nonclassical radical 7; these results merely demonstrate that at least two radical intermediates lead to experimentally significant amounts of the isomeric hydrocarbons.

In principal, the various possibilities may be distinguished by trapping studies of the kind reported here. For example, at arbitrarily high hydrogen-donor concentration, the classical-radical mechanism predicts arbitrarily high ratios of 6:5 starting from 2, but a mechanism involving 7 and 3 predicts a leveling off at the partitioning ratio for 7. Of course, the problem is that arbitrarily high concentrations of triethyltin hydride can not be attained; the neat liquid is only about 5 M. Put another way, involvement of a nonclassical radical can lead to mechanistic expressions involving terms in the hydrogen-donor concentration of higher order than those which appear in eqs. 1.7-2 and 1.7-3. However, unless a hydrogen donor is available which permits much greater degrees of trapping than does triethyltin hydride, such terms may be expected to be dominated by the linear term. Thus, a linear relationship at low trapping does not preclude the existence of higher order terms which would signify a mechanism more complicated than one involving only the classical radicals 3 and 4.

8. Hydrogen Abstraction, Ring Cyclization, and Conversion Reactions

Competition between equilibration of the ring-closed and ring-opened forms of the radical and abstraction of hydrogen from various hydrogen donors passes, at the next level of the reaction mechanism, to competition between hydrogen abstraction and ortho-ring cyclization to the radical 9.

There is no information as to what form(s) of the radical undergoes ring-cyclization, but it seems most reasonable to assume that the classical ring-opened radical is responsible; in this formulation, the ring-cyclization is simply an intramolecular example of the well-known



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addition of alkyl radicals to aromatic systems extensively studied by Szwarc (25).

When the existence of the ring-cyclization process became apparent, that process seemed to offer only wholly lamentable mechanistic complications. Moreover, the high rate of ring-cyclization shortens radical lifetimes to such an extent that only a very few relatively active hydrogen donors can profitably be studied. However, existence of the ring-cyclization has turned out to be advantageous for two

reasons. The first reason is that it provides a point of reference which makes possible the calculation of relative rates of hydrogen abstraction by ring-opened radicals from various hydrogen donors, especially 1,4-cyclohexadiene and triethyltin hydride. We noted earlier (p. 104) that activation energies for at least two rate constants are required to locate the energies of the ring-opened and ring-closed radicals with respect to the transition states indicated in Fig. 10. Measurement of actual rate constants for rapid reactions of steady-state free-radical intermediates is a ticklish problem which is far beyond the scope of instrumentation or techniques available in this research group (44). Therefore, we must rely on appropriate models for estimation of the necessary activation energies. Fortunately, a convenient model process is available for the ring-opened radical: Brown and James have reported an activation energy of 5.8 kcal/mole* for abstraction of hydrogen by ethyl radicals from 1,4-cyclohexadiene in the gas phase (45). Assuming, then, that the same value is appropriate for hydrogen abstraction from 1,4-cyclohexadiene by the ring-opened radical $\underset{\sim}{3}$ (which may behave very much like a typical primary radical), relative rates of hydrogen abstraction from 1,4-cyclohexadiene and triethyltin hydride

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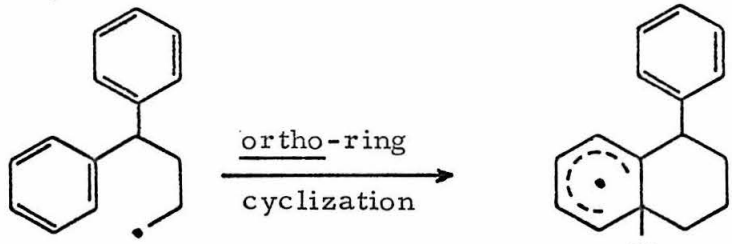
*Actually, this identification requires the assumption that combination and disproportionation of ethyl radicals require no activation energy; the quantity measured experimentally is the ratio of the hydrogen abstraction rate constant divided by the square root of the rate constant for pairwise consumption of ethyl radicals. While the experimental determination of the latter yields a value of 2 ± 1 kcal/mole (46), the reports that combinations of methyl radicals (47), isopropyl radicals (48), and t-butyl radicals (49) require no activation energy suggest that this value is likely to be in error.

at various temperatures suffice to locate the ring-opened radical on the reaction diagram.

The second reason is that comparison of relative rates of ring-cyclization and hydrogen abstraction for the ring-opened radical 3 and the saturated radical 21 (from the saturated perester 8) with appropriate model processes suggests that a common radical intermediate*



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is responsible both for hydrogen abstraction to give 5 and for ring-cyclization. In view of the rather special conformation required for ring-cyclization and the presumption against formation of a nonclassical radical in a bicyclobutonium-type geometry (13), the radical most favorable for ring closure would presumably be the classical ring-opened radical.* Thus, the comparison argues against significant incursion of a species such as the homoallyl-type nonclassical radical 7 which would be capable of giving ring-opened hydrocarbon but not of undergoing ring-cyclization.

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*One of course presumes that the conformations of 3 responsible for ring-cyclization and hydrogen abstraction may be different, but the same should be true in the saturated series.

We need now to consider how relative rate constants for hydrogen abstraction and ring-cyclization can be extracted from the data. If all the ring-opened hydrocarbon is formed from the ring-opened radical, then the rate equation for formation of ring-opened hydrocarbon is

$$d(\underset{\sim}{5})/dt = k_a(ZH)(\underset{\sim}{3}) \quad . \qquad (1.8\text{-}1)$$

(We shall continue to use k_a for hydrogen abstraction by the ring-opened radical. When a particular hydrogen donor is intended, it will be indicated by a superscript, such as k_a^{SnH} for triethyltin hydride and $k_a^{\hexagon}$ for 1,4-cyclohexadiene.) Similarly, the rate equation for <u>formation only</u> of the ring-cyclized radical is

$$d(\underset{\sim}{9})/dt = k_r(\underset{\sim}{3}) \quad . \qquad (1.8\text{-}2)$$

Dividing eq. 1.8-1 by eq. 1.8-2 we get

$$d(\underset{\sim}{5})/d(\underset{\sim}{9}) = k_a(ZH)/k_r \quad . \qquad (1.8\text{-}3)$$

If ring-cyclization is invariably followed by conversion to the ring-cyclized dihydronaphthalene $\underset{\sim\sim}{10}$, we would also have

$$d(\underset{\sim}{5})/d(\underset{\sim\sim}{10}) = k_a(ZH)/k_r \quad . \qquad (1.8\text{-}4)$$

As with eq. 1.7-2, integration of eq. 1.8-4 can be effected by replacing ZH by its average value, provided ZH is substantially in excess. Then the <u>reduced ratio</u> R is given by*

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*As quantities calculated according to eq. 5 will frequently be discussed in this thesis, economy and precision of language dictates the utilization of a special name.

$$R \equiv \frac{(\%\ \text{yield}\ \underset{\sim}{10}) \times (ZH)_{av}}{(\%\ \text{yield}\ \underset{\sim}{5})} \cong k_r/k_a \ . \qquad (1.8\text{-}5)$$

(The quantity R is of special interest because it does not include the explicit strong, but really not very interesting, dependence of the product ratio $\underset{\sim}{10}$:$\underset{\sim}{5}$ on the hydrogen donor concentration. Thus, more subtle effects are made to stand out.)

However, the necessary condition for equating R with k_r/k_a--that ring-cyclized radical $\underset{\sim}{9}$ always go on to give ring-cyclized hydrocarbon $\underset{\sim}{10}$--seems never to be fulfilled experimentally. One possible problem--reversibility of the ring-cyclization--is shown below to be unimportant under conditions employed in this work. But another remains; in conversion to $\underset{\sim}{10}$, the ring-cyclized radical $\underset{\sim}{9}$ must lose a hydrogen atom through disproportionation in a radical-radical reaction. However, such reactions can also lead to combination; or may involve a disproportionation where the ring-cyclized radical receives the transferred hydrogen atom, leading to the tetrahydronaphthalenes $\underset{\sim}{13}$ (see Chart 4, p. 78). Moreover, if each member of a radical pair is a ring-cyclized radical, no more than one of the two can end up as dihydronaphthalene.

Thus, the conversion reactions are expected to be inefficient. As a result, R will underestimate k_r/k_a. This assumes, of course, that neither $\underset{\sim}{5}$ nor $\underset{\sim}{10}$ is destroyed under the reaction conditions. Nonetheless, equating reduced ratios to k_r/k_a may still suffice for a rough guess for the latter.

To do better, we must in some manner estimate the relationship

between the yield of the dihydronaphthalene and that of all naphthalenoid products. This can be done in most cases by direct vpc measurement of the yield of tetrahydronapthalenes and estimation of the amount of dimer likely to be present by consideration of material balances.

This discussion shows that we need to consider the whole of the reaction mechanism in order to extract values of k_r/k_a. The initial phases have been discussed in the subsections above. The remainder will be covered in this subsection on a solvent-by-solvent basis, with the exception of induced decomposition in the presence of triethyltin hydride, which is considered in subsection 9.

A. t-Butyl (γ,γ-Diphenylallyl)peracetate and t-Butyl Diphenylcyclopropylperacetate

(1.) In the Presence of 1,4-Cyclohexadiene

Yields and ratios of products for decomposition of ring-opened perester 1 in the presence of 1,4-cyclohexadiene are given in Table 1. The data at 131° is also shown graphically in Fig. 1. Note that, for runs at any one temperature, the yield of ring-opened hydrocarbon increases, and that of the ring-cyclized hydrocarbon decreases, with increasing cyclohexadiene concentration. The same sort of behavior is observed for decomposition of the ring-closed perester 2 (Table 2 and Fig. 2). The pattern is indicative of a partitioning in which one step (hydrogen abstraction by 3) depends on the cyclohexadiene concentration but the other (ring-cyclization) does not. The identification of 5

and 10 is based on (a) agreement of retention times for independently prepared samples with those of the candidate materials on Ucon polar, silicone oil, and Apiezon L; and (b) observation of distinctive nmr absorbances of the authentic materials in the nmr spectra of chromatographed and distilled reaction mixtures from 'large-scale' perester decompositions like those described on pp. 72-79.

The rightmost column of Tables 1 and 2 gives reduced ratios calculated from eq. 1. 8-5. If conversion of ring-cyclized radicals to dihydronaphthalene were 100% efficient, the numbers tabulated would simply be equal to $k_r/k_a^{\bigcirc}$, a constant at each temperature. However, the numbers are not constant, but tend to increase with cyclohexadiene concentration within each reaction series. If the discussion following eq. 1. 8-5 is correct, the increase reflects an increasing efficiency of conversion of 9 to 10 at higher cyclohexadiene concentrations. The following interpretation is suggested. At higher cyclohexadiene concentrations, ring-opened radicals more frequently abstract hydrogen to give 5 plus a cyclohexadienyl radical, and less frequently undergo ring-cyclization. Therefore, an individual ring-cyclized radical is increasingly likely to meet a cyclohexadienyl radical rather than a second ring-cyclized radical at increased cyclohexadiene concentrations. The fact that the tabulated numbers increase with increasing cyclohexadiene concentration then implies that conversion of 9 to 10 is more likely if the second radical is cyclohexadienyl rather than ring-cyclized. Another possibility is that the rate-constant ratio $k_r/k_a^{\bigcirc}$ is solvent dependent, increasing at higher cyclohexadiene concentrations (see pp. 259–265).

The essential irreversibility of the ring-cyclization can be seen from results given in Tables 4, 5, and 6. The rightmost column of each of these tables again gives reduced ratios calculated from eq. 1.8-5. In Table 4 (for decomposition of the ring-opened perester at 110°), the reduced ratios show little dependence on the initial perester concentration. As discussed in subsection 1, a shift to lower initial perester concentration results in smaller steady-state free-radical concentrations. If the ring-cyclization were reversible, there would then be a greater feed back of ring-cyclized radicals to ring-opened radicals at the lower perester concentrations. The reason is that whereas 'decyclization' is accomplished by a single radical, conversion to napthalenoid products requires a second radical, which will now be present in smaller concentration. As a result, if decyclization were competitive with conversion to naphthalenoid products at the highest perester concentrations in Tables 4 or 6, a substantial decrease would be seen (but is not) in the reduced ratios.

How large 'substantial' might be can be inferred from the variations of the ratio $\underset{\sim}{6}:\underset{\sim}{5}$ with perester concentration in Tables 4 and 6. Like the dihydronaphthalene $\underset{\sim\sim}{10}$, the ring-closed hydrocarbon $\underset{\sim}{6}$ is principally formed by disproportionation of the precursor radical with cyclohexadienyl radical. But unlike the ring-cyclized radical, formation of the ring-closed radical from the ring-opened radical is readily reversible. The ratio $\underset{\sim}{6}:\underset{\sim}{5}$ decreases by a factor of 4 in Table 4 and by a factor of 7 in Table 6 as the initial perester concentration is decreased by factors of 300 and 100, respectively.

The lack of any similar variation in the ratio of $\underset{\sim\sim}{10}$ to $\underset{\sim}{5}$ confirms

the essential irreversibility of the ring-cyclization.* Of course, if we were to continue to decrease the initial perester concentration, and if the only options for ring-cyclized radicals were destruction in radical-radical reactions or decyclization, eventually a point would be reached at which there would be sufficient time for decyclization to occur.

The supposition that most of the ring-closed hydrocarbon is formed via abstraction of hydrogen by ring-closed radical from cyclohexadienyl radical can best be established by consideration of the quantitative accuracy with which the ratios $\underset{\frown}{6}:\underset{\frown}{5}$ can be fit. That consideration is undertaken in Section Two, where it will be shown that the ratios $\underset{\frown}{6}:\underset{\frown}{5}$ and $\underset{\frown}{5}:\underset{\frown\frown}{10}$ from Tables 1, 2, 4, 5, and 6 can be adequately correlated as described above, except that formation of small amounts of ring-closed hydrocarbon via hydrogen abstraction by ring-closed radicals from 1,4-cyclohexadiene must be included in the treatment. Note, for example, that the ratios $\underset{\frown}{6}:\underset{\frown}{5}$ for 0.25 M ring-opened perester at about 9 M cyclohexadiene in Table 1 range from 0.010 to 0.013, while the same quantities (Table 5) at 0.001 M perester are only about 0.004. The significant factor here is the relative smallness of the decrease for the 260-fold variation in the initial perester concentration. It can be shown that at constant 1,4-cyclohexadiene concentration the contribution to the ratio $\underset{\frown}{6}:\underset{\frown}{5}$ arising from formation of $\underset{\frown}{6}$ via hydrogen abstraction from cyclohexadienyl radical should be very nearly exactly proportional to the square root of the initial perester concentration (which varies by a factor of 16).

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*That decyclization is apparently much slower than ring-opening by the ring-closed radical can be shown to be in harmony with the greater exothermicity expected for the ring-cyclization. See the discussion on pp. 287-290.

These observations can be rationalized by the assumption that both hydrocarbons can be formed via hydrogen abstraction from 1,4-cyclohexadiene itself. Therefore, there is a value (equal to the characteristic ratio for hydrogen abstraction from 1,4-cyclohexadiene, see pp. 13, 101) below which the ratio $\underset{\frown}{6}:\underset{\frown}{5}$ can not fall.

Actually, because some formation of $\underset{\frown}{6}$ via hydrogen abstraction from cyclohexadienyl radical still occurs at 0.001 M perester, the characteristic ratio for 1,4-cyclohexadiene at 100° is about 0.0035, slightly lower than the observed $\underset{\frown}{6}:\underset{\frown}{5}$ ratio of 0.040.

One experimental problem must be confessed here. The run at 99° listed in Table 5 gave a ratio $\underset{\frown}{6}:\underset{\frown}{5}$ of approximately 0.1 when initially analyzed on the standard Ucon polar column. Note that this ratio is an order of magnitude higher than that quoted in Table 1 for 0.26 M ring-opened perester. However, the retention time of 'diphenylcyclopropylmethane' relative to diphenylbutene was about 4% lower than expected. On reinvestigation using a silicone oil column, the apparent ratio fell to 0.014. For good measure, the two columns were then joined together and the analysis repeated. The value quoted in Table 5 (0.0040) was now obtained, and the retention times of both candidate and authentic diphenylcyclopropylmethane were found to be 56.1 min. The other runs reported in Table 5 were analyzed only on the combined silicone oil--Ucon polar column.

Clearly, something is amiss. It was subsequently found that degassed samples of Aldrich 1,4-cyclohexadiene, whether taken from a newly opened bottle or one open for several weeks, and whether freshly distilled or not, develop upon heating one or more impurities which

have very nearly the retention time of 6 on Ucon polar. From the retention time, the material(s) would seem to be trimeric, or C_{18}. Strangely, no other materials of comparable or longer retention time seem to be formed, and the yield of dimeric material is much smaller than that of the presumed trimer.

As Aldrich 1,4-cyclohexadiene routinely contains 1,3-cyclohexadiene in the amount of 0.01--0.1%, a possible mechanism for formation of the presumed trimer would be Diels-Alder addition of 1,4-cyclohexadiene to 1,3-cyclohexadiene, followed by addition of the adduct to a second molecule of 1,3-cyclohexadiene. However, no correlation between initial 1,3-cyclohexadiene concentration and yield of the presumed trimer was found for three samples (degassed; maintained at 135° for 25 hr) which were approximately 1%, 0.1%, and 0.02% 1,3-cyclohexadiene in 1,4-cyclohexadiene. The last of these samples was freshly distilled material. The concentrations of presumed trimer (assuming unexceptional vpc response characteristics) after heating were roughly 0.01 mg/ml, 0.022 mg/ml, and 0.008 mg/ml, respectively. These concentrations would be interpreted as yields of 6 of roughly 5%, 11%, and 4% for an initial concentration of ring-opened perester 1 of 0.001 M, but only 0.02%, 0.04%, and 0.015% for 0.26 M 1.

As yields of 6 for decomposition of 0.26 M 1 in neat 1,4-cyclohexadiene are 0.3--0.4%, apparent yields of 6 reported in Table 1 are probably not significantly distorted by any solvent-derived impurity which may be present. This is an important point because of the possibility the remaining small amounts of 6 detected by vpc analysis

on the combined column for the runs of Table 5 might simply arise from an especially intelligent impurity. Fortunately, the calculations of Section Two (pp. 273-275) demonstrate that even for the runs of Table 1 a characteristic ratio of about 0.004 must be assumed for hydrogen abstraction from 1,4-cyclohexadiene to quantitatively reproduce the ratio data for $\underset{\wedge}{6}:\underset{\wedge}{5}$.

Although the situation is a good deal muddier than one would like, we shall adopt the position that hydrogen abstraction from 1,4-cyclohexadiene to give ring-closed hydrocarbon $\underset{\wedge}{6}$ does occur to a measureable extent and has in fact been characterized experimentally.

The mechanistic evaluation of Section Two indicates that the characteristic ratio for 1,4-cyclohexadiene is slightly temperature dependent, lower temperatures corresponding to larger $\underset{\wedge}{6}:\underset{\wedge}{5}$. This means that the transition state for formation of the ring-closed hydrocarbon lies below that for formation of the ring-opened hydrocarbon. Various new relationships are shown in Fig. 10, where the estimate of 5.8 kcal/mole for hydrogen abstraction by ring-opened radical from 1,4-cyclohexadiene (see p. 108) has been employed.

The much greater yields of the ring-closed hydrocarbon observed for decomposition of $\underset{\wedge}{2}$ (compare Tables 1 and 2 or Figures 1 and 2) comes about essentially as follows.

The half-life for decomposition of ring-opened perester $\underset{\wedge}{1}$ at 131° is about the same as that for $\underset{\wedge}{2}$ at 35°; therefore, because termination reactions of cyclohexadienyl radicals are expected to have little or no activation energy, the steady-state cyclohexadienyl radical concentration

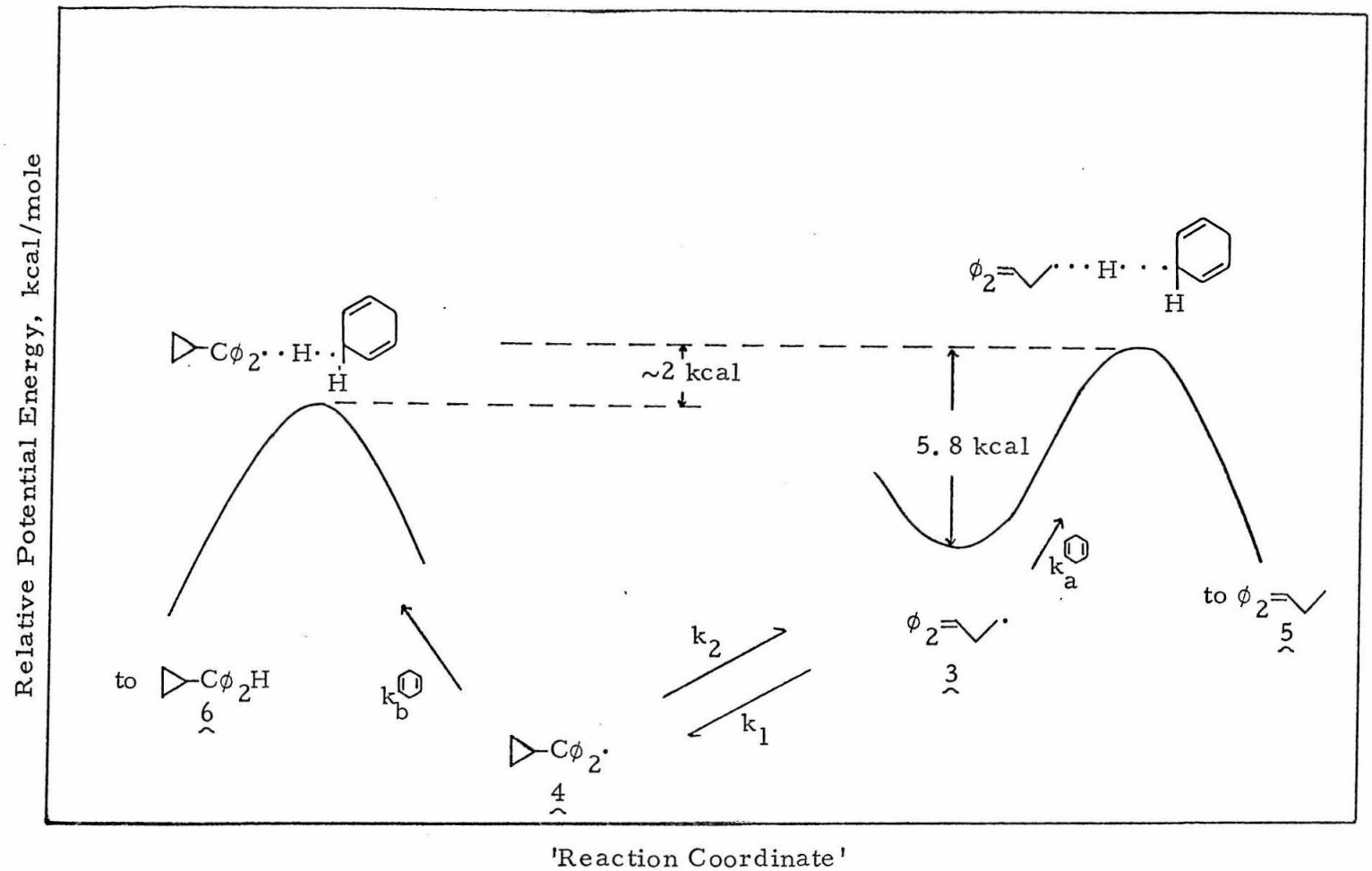

Figure 11. Some relative energies for hydrogen abstraction by the ring-opened and ring-closed radicals (3 and 4) from 1,4-cyclohexadiene.

goes roughly as the square root of the decomposition rate. However, the steady-state concentration of the ring-closed radical $\underset{\wedge}{4}$ will be quite different at the two temperatures. As $\underset{\wedge}{4}$ is more stable than the ring-opened $\underset{\wedge}{3}$ (see pp. 277-279), the ratio of $\underset{\wedge}{3}$ to $\underset{\wedge}{4}$ will be greater at the higher temperature. The rates of hydrogen abstraction from 1,4-cyclohexadiene to give $\underset{\wedge}{5}$ and ring-cyclization to give $\underset{\wedge}{9}$ will then be much faster at 131° due both to the temperature effect on $k_a^{\textcircled{1}}$ and k_r and to the greater relative amount of $\underset{\wedge}{3}$. As a result, the steady-state concentration of ring-closed $\underset{\wedge}{4}$ will be much smaller at 131° than at 35°, and the amount of ring-closed hydrocarbon can be correspondingly less, even if the rate constant for hydrogen abstraction by $\underset{\wedge}{4}$ from cyclohexadienyl radical is somewhat greater at 131°.

Another important phenomenon--the almost nonexistent temperature dependence of the ratio $\underset{\wedge}{6}:\underset{\wedge}{5}$ for closely similar cyclohexadiene concentrations (see Table 2)--comes about, broadly speaking, through the accidental cancellation of large changes in two of the factors involved in the discussion in the previous paragraph: increasing the temperature increases the rate of the perester decomposition (thus increasing the cyclohexadienyl radical concentration and favoring formation of $\underset{\wedge}{6}$ over $\underset{\wedge}{5}$); but decreases the ratio of ring-closed to ring-opened radical (thus favoring $\underset{\wedge}{5}$ over $\underset{\wedge}{6}$). Indeed, approximate dissection in Section Two of the overall effect into these two factors will make it possible to place the ring-closed radical on the reaction diagram with respect to the ring-opened radical and the various hydrogen-abstraction transition states.

To complete the description of the reaction mechanism for decomposition of the peresters $\underset{\sim}{1}$ and $\underset{\sim}{2}$ in 1,4-cyclohexadiene, we need to consider the products designated by letters, rather than by numbers and structures, in Tables 1, 2, 4, and 6. The product called $\underset{\sim}{B}$ was previously considered when formation of cage products was under discussion (pp. 71-81). Little need be said here, except perhaps to remind the reader that $\underset{\sim}{B}_1$ of Table 6 (perester $\underset{\sim}{2}$ at various concentrations), a part of $\underset{\sim}{B}$ in Table 2, and most or all of $\underset{\sim}{B}$ in Tables 1 and 4 was attributed to a tetrahydronaphthalene product or to isomeric tetrahydronaphthalenes (see Chart 4, p. 78). A principal reason for this assignment was that yields of $\underset{\sim}{B}$ in Table 1 strongly parallel those of the dihydronaphthalene $\underset{\sim\sim}{10}$. Additional support for this assignment will be given later in the present subsection when we consider decomposition of the peresters in poorly hydrogen-donating solvents (pp. 126-131) and in Section Two, where yields of $\underset{\sim}{B}$ will be calculated and compared with those measured experimentally (pp. 281, 282).

The product $\underset{\sim}{A}$ may be benzophenone. The first suggestion that this might be so came about as the result of the following observations. If one takes a sample of $\underset{\sim}{1}$ repeatedly recrystallized from pentane (and therefore presumably pure) and places it on a lab bench, uncovered or capped in a brown jar, in the course of one or two months the crystalline perester turns to a pale yellow slime, the principal constituent of which is benzophenone (identified by mass spectroscopy, infrared, and nmr). While the relevance of this observation to degassed thermal decomposition may be questionable, it does indicate that a mechanism exists for transforming the perester into benzophenone. What that

mechanism is, I do not know, and offer here on speculation.

No attempt was made to isolate benzophenone from actual reaction mixtures, although it should not be difficult to do so. The evidence that A is benzophenone comes from vpc retention time measurements. On a column composed of a 12-ft. section of silicon oil followed by 6-ft. of Ucon polar, both benzophenone and a peak of about the correct area for A in the 110° run of Table 5 had retention times of 58.8 min. On Ucon polar alone, strong overlapping of the A and B peaks for the 0.27 M run of Table 4 made it impossible to determine with certainty the retention time of the A peak, but it is within 2% of that observed for benzophenone. Of course, benzophenone might have been a contaminant of the perester (presumably present in varying amounts), but arguing against this possibility is the fact that the 1.8% yield for 0.27 M 1 in 1.1 M 1,4-cyclohexadiene at 110° (Table 4) agrees well with the 2.0% yield from Table 1 for 0.28 M perester from another batch at 1.1 M 1,4-cyclohexadiene at 99°.

The average of the subtotal yields in Table 1 and the total yields in Table 4 is 66%. Adding to this figure 15% for the yield of the lactone 23 (see subsection 6) gives an average material balance of about 80% for decomposition of ring-opened perester in the presence of 1,4-cyclohexadiene. For the ring-closed perester, the average total yield for Table 2 is 90%. For Table 6, we have previously (p. 78) argued that, possibly due to an acid-producing impurity in the perester sample used, the anticipated 20 to 25% of ring-closed ether does not survive the reaction conditions. Taking this into account, the observed average total yield of about 69% should be corrected to about 90%. Thus,

on the average, material balances are 80% for the ring-opened perester and 90% for the ring-closed perester. While the remainder need not be dimer containing napthalenoid residues from termination reactions of the ring-cyclized radicals,* these considerations would suggest that not more than 10 to 20% of unobserved dimeric products are produced. The average yield of dihydronaphthalene is about 17% and the average for tetrahydronaphthalene, judging from yields of $\underset{\sim}{B}$ in Tables 1 and 4 and of $\underset{\sim}{B}_1$ in Table 6, is about 9%. Thus, dihydronaphthalene probably accounts for about a third to a half of the ring-cyclized radicals.

Of course, the analysis given above is only approximately correct. An alternative approach--comparison on a run-by-run basis of the yield of the dihydronaphthalene with that measured for the tetrahydronaphthalene(s) and indicated by the material balance for dimeric products--is unattractive in view of the appreciable experimental error in product yields which is reflected by the magnitudes of largely random fluctuations in total yields from run to run. Unreliability of absolute yields arising from imprecise measurement of amounts of perester and internal standard taken has been mentioned previously (pp. 46-47); the procedure used here assumed that averaging absolute

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*Addition of radicals to 1,4-cyclohexadiene might lead to materials which would not be observed by vpc. An indirect test of this possibility was made in a run in 1,4-cyclohexadiene to which 0.6 M 1,3-cyclohexadiene has been added (row 7, Table 8). Addition of methyl radicals to 1,3-cyclohexadiene proceeds possibly two orders of magnitude more rapidly than addition to the unconjugated 1,4-isomer (84). If, therefore, addition of hydrocarbon radicals to 1,4-cyclohexadiene occurs to any measurable extent, the material balance for the run in the presence of 1,3-cyclohexadiene should be noticeably low. Comparison with similar runs from Table 1 shows that this is not the case.

yields over large numbers of runs will tend to average errors arising from that source.

Detailed translation of these considerations of average efficiencies for conversion of ring-cyclized radicals to dihydronaphthalene to reliable estimates for k_r/k_a⬡ will be undertaken in Section Two. It will be possible there to predict yields of tetrahydronaphthalene and of dimer as a function of parameters describing the conversion efficiency. Those parameters will then be chosen to reproduce tetrahydronaphthalene and dimer yields on the scale suggested by the above considerations.

Even at this point, however, we can get an approximate measure of the value of k_r/k_a⬡. As calculated from eq. 1.8-5 (i.e., assuming 100% conversion of ring-cyclized radicals to dihydronaphthalene), the value of k_r/k_a⬡ obtained by averaging over Tables 1, 2, 4, and 6 is about 2.6. If the average conversion efficiency is 40%, then the estimated value of k_r/k_a⬡ near the middle of the temperature range (i.e., between 70 and 100°) becomes 6.5. In addition, k_r/k_a⬡ is temperature dependent, as can be seen in the following way. According to eq. 1.8-5, the hydrogen-donor concentration at which the yields of the ring-opened and ring-cyclized hydrocarbons are equal is a measure of k_r/k_a⬡. At 131°, that concentration (see Figure 1) is 2.6 M. At 35° (Figure 2), the yields cross at about 1.8 M. The initial 1,4-cyclohexadiene concentrations in each case must be corrected to average values with reference to the initial perester concentration and the reaction stoichiometry, but those corrections do not alter the apparent trend to higher values at higher reaction temperatures. Therefore, the activation energy for ring-cyclization is slightly greater than that for hydrogen abstraction

from 1,4-cyclohexadiene by ring-opened radical.

We shall adopt here, from Section Two (p. 272), the relationship

$$k_r/k_a^{\bigcirc} = 20 \exp(-0.8/RT) \quad . \qquad (1.8\text{-}6)$$

(2.) In Indene

Results for decomposition of peresters $\underset{\sim}{1}$ and $\underset{\sim}{2}$ in indene are summarized in Table 7. Several major departures from the pattern of results with 1,4-cyclohexadiene may be noted. Yields of the ring-opened hydrocarbon are only about 10% for neat indene, in contrast to yields of 30--40% for neat 1,4-cyclohexadiene. This divergence in yields is reflected in the values of the reduced ratios calculated from eq. 1.8-5, which are approximately 10 in the presence of indene and 2.6 in the presence of 1,4-cyclohexadiene.

The overall yields are 46 and 49% for decomposition of $\underset{\sim}{1}$, and 39 and 37% for decomposition of $\underset{\sim}{2}$. Even adding a presumed 15% for the yield of the lactone $\underset{\sim}{\underset{\sim}{23}}$ for decomposition of $\underset{\sim}{1}$ and assuming that the low yields of $\underset{\sim}{B}$ for the ring-closed perester result from at least partial destruction of the usual 20 to 25% of ring-closed ether, the resulting material balances of about 63% for $\underset{\sim}{1}$ and 60% for $\underset{\sim}{2}$ are rather low. If the difference between these quantities and 100% represents dimeric naphthalenoid products,* the efficiency of conversion of ring-cyclized radicals to dihydronaphthalene would be about 1/3, and the adjusted

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*Higher molecular weight products may also be produced via addition of the ring-opened radical $\underset{\sim}{3}$ to indene. For methyl radicals, addition to, and hydrogen abstraction from, indene occur with equal facility (85).

value of k_r/k_a^{indene} would be about 30, indicating that $k_a^{\bigcirc}/k_a^{indene}$ is about 30/6.5 = 5.

Yields of the ring-closed hydrocarbon are much lower than for decomposition of the peresters in 1,4-cyclohexadiene. This is consistent with the supposition that most of the ring-closed hydrocarbon is produced in cyclohexadiene via abstraction of hydrogen by ring-closed radicals from cyclohexadienyl radical, for indenyl radicals can not function as hydrogen donors. The principal hydrogen donor for formation of the 0.3--0.5% $\underset{\frown}{6}$ for decomposition of $\underset{\frown}{2}$ in indene is likely to be the ring-cyclized radical. On this basis, the lesser amounts of $\underset{\frown}{6}$ for decomposition of $\underset{\frown}{1}$ arise much in the same way as the disparity in amounts of $\underset{\frown}{6}$ for ring-opened and ring-closed perester in cyclohexadiene (pp. 118, 120).

(3.) In Poorly Hydrogen-Donating Solvents

By 'poorly hydrogen-donating solvents' is meant those in which ring-cyclization by the ring-opened radical is much faster than hydrogen abstraction from solvent. Data may be found in the upper bank of four runs in Table 8 for the ring-opened perester, and in Table 9 for the ring-closed perester. The solvents investigated are cyclohexane, diethyl ether, tetrahydrofuran, cumene, benzene, and tetraethyltin. Over this range of solvents, the yield of the ring-opened hydrocarbon $\underset{\frown}{5}$ varies only from 0.4% for a benzene run to 2% for an ether run. Fully 7 of the 13 reported yields are either 1.0 or 1.1%.

This similarity in the yields of $\underset{\frown}{5}$ requires some comment. Two possibilities are apparent: either all of the solvents employed happen

to be nearly equally reactive toward the ring-opened radical; or materials developed in the course of the reaction (such as dihydro- and tetrahydronaphthalenes) are the active hydrogen donors. Estimation of k_r/k_a for some of the poorly hydrogen donating solvents would provide the most direct way of assessing the reasonableness of the first alternative.

We can proceed as follows for reaction in cyclohexane. From data given by Boddy and Steacie (54), we can calculate

$$k_{a'}^{\bigcirc}/(k_t)^{\frac{1}{2}} = 10^{-7.2} \exp(-10.1/RT)(\text{cc-molecule}^{-1}\text{-sec}^{-1})^{\frac{1}{2}} , \qquad (1.8\text{-}7)$$

where $k_{a'}^{\bigcirc}$ denotes the rate constant for abstraction of hydrogen by d_5-ethyl radicals from cyclohexane, and k_t denotes the rate constant for bimolecular combination plus disproportionation of the d_5-ethyl radicals. For hydrogen abstraction by (undeuterated) ethyl radicals from cyclohexadiene, Brown and James (45) give

$$k_{a'}^{\bigcirc\!\!\bigcirc}/(k_t)^{\frac{1}{2}} = 10^{-7.3} \exp(-5.8/RT)(\text{cc molecule}^{-1}\ \text{sec}^{-1})^{\frac{1}{2}} . \qquad (1.8\text{-}8)$$

As only secondary deuterium isotope effects are involved, and as these should be small (55), approximate relative rates for hydrogen abstraction by ethyl radicals from 1,4-cyclohexadiene and cyclohexane can be obtained by dividing eq. 1.8-8 by eq. 1.8-7.

$$k_{a'}^{\bigcirc\!\!\bigcirc}/k_{a'}^{\bigcirc} = 0.8 \exp(4.3/RT) . \qquad (1.8\text{-}9)$$

As ethyl-radical reactivities should be an excellent model for ring-opened radical reactivities, eqs. 1.8-6 and 1.8-9 can be combined

to give

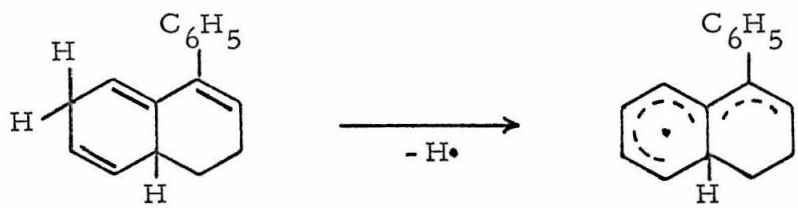
$$k_r/k_a^{\bigcirc} = 16 \exp(3.5/RT) \quad . \qquad (1.8\text{-}10)$$

Values of this quantity are 6×10^3 at 35° and 1.5×10^3 at 131°. Since neat cyclohexane is about 10 M, the total naphthalenoid products to ring-opened hydrocarbon is estimated to be 600:1 at 35° and 150:1 at 131°. Finally, if the total yield of naphthalenoid products plus ring-opened 5 is 60% at each temperature, yields of ring-opened hydrocarbon arising via abstraction of hydrogen from cyclohexane would be about 0.1% at 35° and 0.4% at 131°.

From Tables 8 and 9 we see that yields up to an order of magnitude greater are in fact found: 0.5 to 1.1% at 35°, depending on the initial perester concentration; and 1.0% at 131°. Two things may be said. Firstly, the estimated magnitudes of $k_r/k_a^{\bigcirc}$ suggest that only a part of the diphenylbutene observed can be attributed to abstraction of hydrogen from cyclohexane by 3. Secondly, even if the various approximations employed have introduced considerable error into the equation for $k_r/k_a^{\bigcirc}$, a major result--namely that $k_r/k_a^{\bigcirc}$ must be appreciably temperature dependent--should stand. Thus, hydrogen abstraction solely from cyclohexane would not be expected to give such similar yields of 5 at the two temperatures.

Both the observed yields and the lack of any appreciable temperature dependence therefore suggest the existence of alternative hydrogen donors. The ring-cyclized hydrocarbon 10 is a possible candidate. However, the 'best-looking' radical it could yield would presumably be endowed with less resonance stabilization than is possessed by the

indenyl radical, for the radical from 10 would have an additional, conjugation-breaking methylene group. The (isomeric) tetrahydronaphthalenes (see Chart 4, p. 78) which could yield radicals with more extensive pi-systems, and therefore greater resonance stabilization, than cyclohexadienyl radicals, would seem to be more likely possibilities.



B (one possibility) 9

The situation may be rather similar in ether, tetrahydrofuran, cumene, and tetraethyltin. Model reactions involving methyl radicals (56) and phenyl radicals (86) suggest that cyclohexane, ether, and cumene should be of similar reactivity towards primary radicals. Tetrahydrofuran should be similar to diethyl ether for structural reasons, and tetraethyltin, having 8 secondary and 12 primary hydrogens, could well be similar in reactivity to cyclohexane. Benzene might be a special case, for radical addition yields a cyclohexadienyl-type radical which might give rise to ring-opened hydrocarbon through hydrogen donation, or might dimerize to give reactive cyclohexadienyl-type products.

Yields of B for decomposition of the ring-opened perester are 2.7% in cyclohexane, 2.5% in ether, and 1% in tetrahydrofuran. All of

these yields are much lower than the 5 to 16% observed in the presence of 1,4-cyclohexadiene. This disparity is at least qualitatively in agreement with the suggestion that B consists of tetrahydronaphthalenes (except for decomposition of perester 2, where the cage ring-closed ether 15 and methylenecyclopropane 16 contribute). Assuming that tetrahydronaphthalenes can still be formed (presumably via disproportionation of pairs of ring-cyclized radicals) under the conditions being surveyed, the high activity as hydrogen donors predicted above would ensure extensive destruction at the hands, especially, of t-butoxy radicals or their successors (methyl radicals or solvent radicals).

Yields of the ring-closed hydrocarbon 6 tend to be much larger in the decomposition of the ring-closed perester than in that of the ring-opened perester. This circumstance is reminiscent of results obtained in the presence of 1,4-cyclohexadiene, and can be explained in a similar fashion. In this case, the role of the cyclohexadienyl radical would be played by the ring-cyclized radical or solvent radical, such as cyclohexyl, cumyl, and so on.

Yields quoted for 6 are 0.2% or less for decomposition of 1, except for the run in ether (0.6%). However, the higher apparent yield in ether does not necessarily indicate some special feature of ether which permits facile hydrogen donation to the ring-closed radical; while the relative retention time on Ucon polar of the vpc peaks attributed to 5 and 6 was correct, the spread between the peaks was about 3% greater on a silicone oil column (an easily observable difference) than that of the authentic materials. In contract, relative retention times were correct both on Ucon polar and on silicone oil for the run in

cyclohexane, where a 'normal' yield of $\underset{\sim}{6}$ is reported.

The much higher yields quoted for $\underset{\sim}{6}$ in Table 9 were obtained by vpc analysis on Ucon polar, except for the first of the two runs in benzene, where a crude analysis by nmr gave roughly the same figure (87). Assuming that the quoted yields are correct, one important question which arises in Section Two needs to be investigated: do the comparable yields of $\underset{\sim}{6}$ observed for decomposition of $\underset{\sim}{2}$ in the presence of 1,4-cyclohexadiene and in the poorly hydrogen-donating solvents indicate that disproportionation of the ring-closed radical $\underset{\sim}{4}$ with the ring-cyclized radical $\underset{\sim}{9}$ is an important reaction at the perester concentrations studied? Evidence that such a reaction is relatively unimportant has previously been considered in the results of decomposition of $\underset{\sim}{2}$ in indene, where an alternative route for formation of $\underset{\sim}{6}$--disproportionation of $\underset{\sim}{4}$ with solvent radical--is disallowed because indenyl radicals can not function as hydrogen donors. As a result, the yield of $\underset{\sim}{6}$ falls to only 0.3-0.5%. By inference, then, the appreciable amounts of $\underset{\sim}{6}$ found for decomposition of $\underset{\sim}{2}$ in cyclohexane, ether, etc., are principally due to hydrogen abstraction from solvent-derived radicals, such as cyclohexyl, etc.

(4.) In Triethyltin Hydride

The purpose of this subsection is to develop an equation for k_r/k_a^{SnH} for use (a) in conjunction with the analogous equation for 1,4-cyclohexadiene to establish a bridge between the energy-level placements of Figs. 10 and 11, and (b) to help to predict the effect of the

reaction stoichiometry on the competition between normal and induced decomposition of 1 in the presence of triethyltin hydrice (subsection 9).

Examination of entries in Tables 1 and 10, or of Figs. 1 and 4 which follow those tables, shows that the competition between ring-cyclization and hydrogen abstraction by ring-opened radicals is rather different in 1, 4-cyclohexadiene and in triethyltin hydride. For example, the hydrogen-donor concentration at which rising yields of ring-opened hydrocarbon and falling yields of ring-cyclized hydrocarbon intersect is 3.2 M for 1, 4-cyclohexadiene (Fig. 1) but only 0.06 M for triethyltin hydride (Fig. 4). This comparison indicates that triethyltin hydride is more active than 1, 4-cyclohexadiene toward the ring-opened radical by approximately a factor of 50 at 125—131°. This calculation of course assumes that the efficiency of conversion of ring-cyclized radicals to dihydronaphthalene is the same in the two situations.

The greater activity of triethyltin hydride also shows up in the characteristic ratios (6:5), which are about 0.07 for triethyltin hydride and 0.0035 for 1, 4-cyclohexadiene at 110°. Thus, the former is more reactive than the latter toward ring-closed radicals by roughly a factor of 20 × 50 = 1000. The pattern--larger response to increased hydrogen-donor activity by the less reactive radical--is as expected.

Extraction of reliable values of k_r/k_a^{SnH} requires some means of assessing the efficiency of conversion of ring-cyclized radicals to the ring-cyclized hydrocarbon. The procedure used for cyclohexadiene--averaging material balances over a large number of runs to take formation of dimers into account, etc. --can not be used here, in part because material balances are only rarely available. However, an

additional factor comes to our aid: successful treatment of induced decomposition in triethyltin hydride from a mechanistic point of view requires the assumption that ring-cyclized radicals react only rarely with triethyltin radicals (see subsection 9). Thus, 10 must be formed mostly by reaction of pairs of ring-cyclized radicals, and because at most one of each pair can be converted to 10, the maximum conversion efficiency is 50%. This explanation is largely substantiated by yields of B (see Chart 4, p. 78), although for some reason those yields do seem consistently smaller than those of 10 (see Table 10).

Because dimers apparently are formed in 1,4-cyclohexadiene, where ring-cyclized radicals react either with cyclohexadienyl radicals or with other ring-cyclized radicals (which may be thought of as substituted cyclohexadienyl radicals), it seems likely that dimers are formed in triethyltin hydride as well. Thus, though the procedure is somewhat arbitrary, I have assumed in the following that the conversion efficiency of 35% is appropriate for reaction in the presence of triethyltin hydride.

The assumed 35% efficiency is in reasonable agreement with material balances. For the 110° run at 0.01 M tin hydride (row 1 of Table 10), the material balance is 81%. Apart from the possibility of experimental error, the discrepancy may be attributed to the yield of the lactone 23 and/or to the formation of naphthalenoid dimers. As explained earlier (p. 85) special conditions are necessary to observe the lactone 23. Those conditions were not employed for the tin hydride runs. If, however, the suggestion is correct that 23 arises via molecule-induced decomposition (subsection 6), its yield would be

expected to fall off with increasing incursion of radical-induced decomposition. From the observed yield of 3.3% for the cage ether 12, the percent normal decomposition is only about 25% (see pp. 152–155). Thus the expected yield of 23 would be ~4%, rather than the 15% observed in 1,4-cyclohexadiene. That still leaves about 15% for the possible yield of dimers, from which the total yield of naphthalenoid products is 17 + 13 + 15 = 45%, and the conversion efficiency is 17/45 × 100 = 38%.

If yields of tin ester 14 for otherwise identical conditions are the same at 110 and 125°, the 0.01 M run at 125° also would support a conversion efficiency of about 35%. Further assuming that the yields of B will fall off at 125° as in the bank of runs at 144° (the vpc spectra for the four 125° runs were lost before yields of B had been extracted), the material balance for the 125° run at 0.044 M tin hydride is also consistent with a conversion efficiency of about 35%. However, the size of possible experimental error in individual runs is indicated by the results of a similar treatment of the 0.39 M tin hydride run at 125°; that treatment indicates a conversion efficiency of about 20%.

Thus, we will assume that k_r/k_a^{SnH} can be obtained by multiplying the reduced ratios calculated from eq. 1.8-5 (rightmost column of Table 10) by 1.0/0.35. However, one problem remains: as is clearly shown by the banks of runs at 125 and 144°, the reduced ratios decrease with increasing tin hydride concentration. This behavior might be due to preferential hydrostannation (41) of 10 or to a change in the pattern of the conversion reactions, as would for example be effected by increasing abstraction of hydrogen by ring-cyclized radicals from triethyltin hydride at the higher tin hydride concentrations. In fact, the

latter explanation will be invoked in the subsequent mechanistic treatment of radical-induced decomposition in triethyltin hydride.

Whatever the perturbing factor, its influence would seem most likely to be minimal at low tin hydride concentrations. Accordingly, (linear) extrapolation to zero tin hydride concentration gives reduced ratios of 0.063 at 125° and 0.082 at 144°. The tin hydride concentration for the single run at 110° is so small (0.01 M) that no extrapolation would be needed. (In the extrapolation procedure at 125°, the run at 0.93 M tin hydride was neglected; the downturn in the yields of 5 and 6 between 0.38 M and 0.93 M indicates the emergence of a new factor, possibly involving hydrostannation of the perester itself as well as of various reaction products.)

Values of k_r/k_a^{SnH} calculated from these reduced ratios assuming a conversion efficiency of 35% (0.15 at 110°, 0.18 at 125°, and 0.23 at 144°) are plotted according to the Arrhenius equation in Fig. 12. The fourth point in that figure, the one at lower right, represents the k_r/k_a^{SnH} value at 35° obtained in the following way from the data of Table 11. Note, in Table 11, that the reduced ratios increase strongly with increasing triethyltin hydride concentration, rather than decreasing as in Table 10. A possible meaning of this trend can be inferred from the fact that the yields of 10 at 35° do not go to zero at the higher tin hydride concentrations as strongly as would be expected, but seem to level off at about 0.7%. Although absolute yields are unavailable at 10°, the reduced ratios again suggest that a similar thing is happening.

In making up the reaction tubes for the runs at 10 and 35°, the perester was first dissolved in benzene or n-octane. Aliquots of the

resulting solution were then pipetted into reaction vessels which were then quickly cooled in Dry Ice-acetone. As the ring-closed perester is not readily soluble at the concentrations listed in either solvent, some time is required to effect solution. Judging from results in benzene or cyclohexane (Table 9), if 3% of the perester decomposed during the preparation and dispensing of the solution, a yield of about 0.7% of 10 would be accumulated. Since at room temperature (23°) the half-life of 2 is about 100 min (p. 237), a preparation time of about 6 minutes would thus explain the failure of 10 to go to zero yield at the higher tin hydride concentrations. No measure of the actual time was made, but it could well have been about that long.

This suggests that a constant amount be subtracted from observed yields of 10 at 35° and the reduced ratios be recalculated. Subtraction of 0.5% gives reasonably constant values of 0.015, 0.012, 0.013, and 0.015, for an average of 0.014. To convert the 0.014 to a k_r/k_a^{SnH} value, an estimation of the efficiency of conversion of ring-cyclized radicals to dihydronaphthalene 10 is again required. Since no experimental information on that efficiency is available for these conditions, the value of 35% inferred at higher temperature has again been employed to give k_r/k_a^{SnH} (35°) = 0.040, the value employed in Fig. 12.

The straight line in Fig. 12 is quite good. It is perhaps especially significant that the three points determined at 110 to 144° lie well on the line, in spite of the narrowness of that temperature range. The least-squares equation for the line is found to be*

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*The standard error in the activation energy was calculated to be 0.7 kcal/mole. This result assumes that the conversion efficiency does not vary by more than 20% (relative) between 35 and 144°.

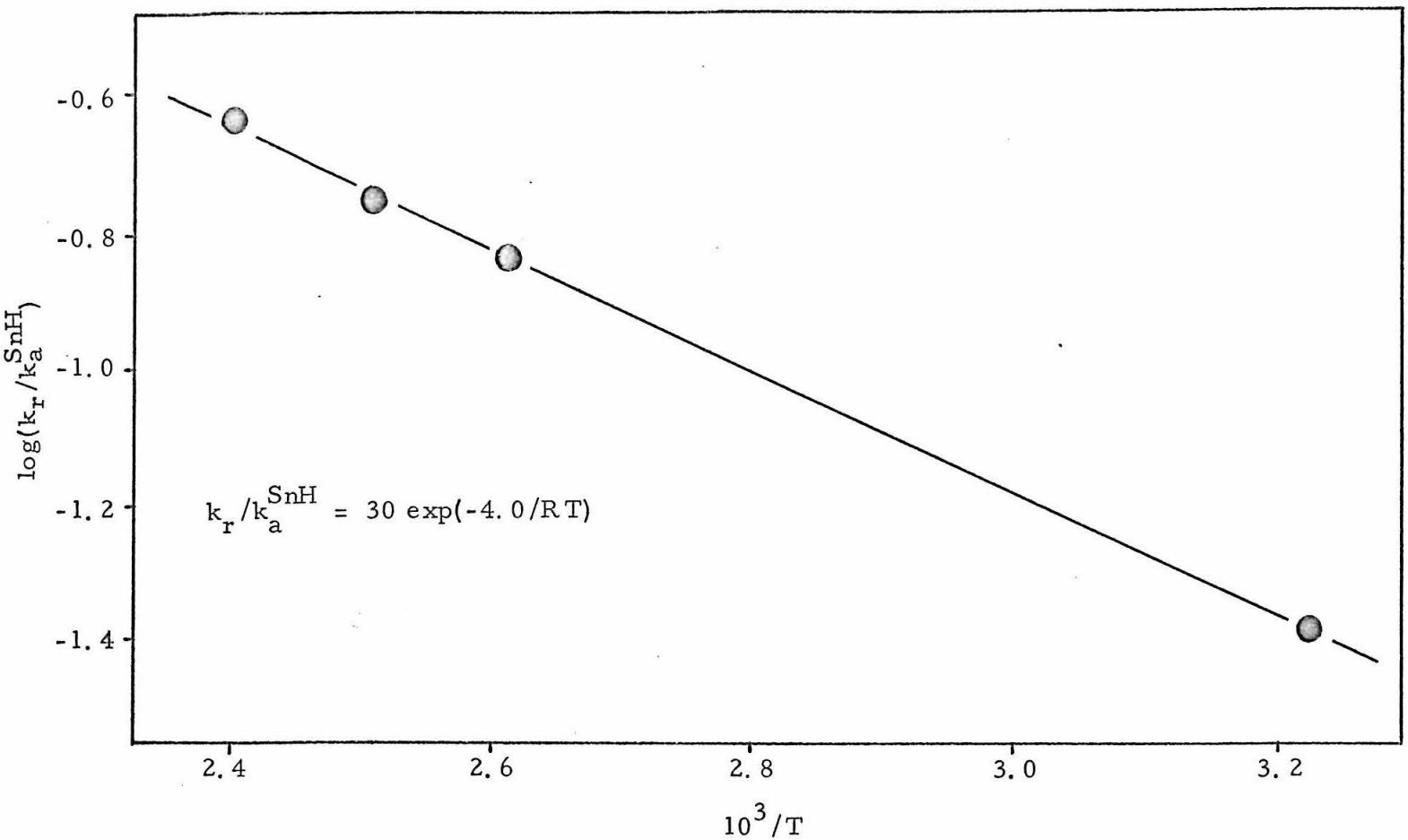


Figure 12. Arrhenius plot for k_r/k_a^{SnH}.

$$k_r/k_a^{SnH} = 30 \exp(-4.0/RT) \quad . \qquad (1.8\text{-}11)$$

Combined with eq. 1.8-6 for $k_r/k_a^{\bigcirc}$, we estimate

$$k_a^{SnH}/k_a^{\bigcirc} = 0.7 \exp(+3.2/RT) \quad , \qquad (1.8\text{-}12)$$

Thus, the activation energy for hydrogen abstraction from 1,4-cyclohexadiene by the ring-opened radical is about 3 kcal/mole greater than from triethyltin hydride. This information allows us to correctly superpose the reaction diagram figures 10 and 11. The result is Fig. 13 (where indicated energies have not yet been rounded to conform to reasonable estimates of experimental accuracy, this to encourage the reader to trace the implications of the superposition). We now can estimate that isomerization of the ring-opened radical to the ring-closed radical requires an activation energy of approximately 4 kcal/mole. In addition, the transition state for formation of the ring-closed hydrocarbon via hydrogen abstraction from triethyltin hydride is actually indicated to be lower in energy than the ring-opened radical itself; if the activation energy for that hydrogen abstraction process is 5--10 kcal/mole, the difference in energy of the two forms of the radical would be of similar magnitude.

B. t-Butyl 5,5-Diphenylperpropanoate

This perester differs structurally from the ring-opened perester in having a carbon-carbon single bond where the latter has a double bond. Reaction steps for processes in the decomposition of the

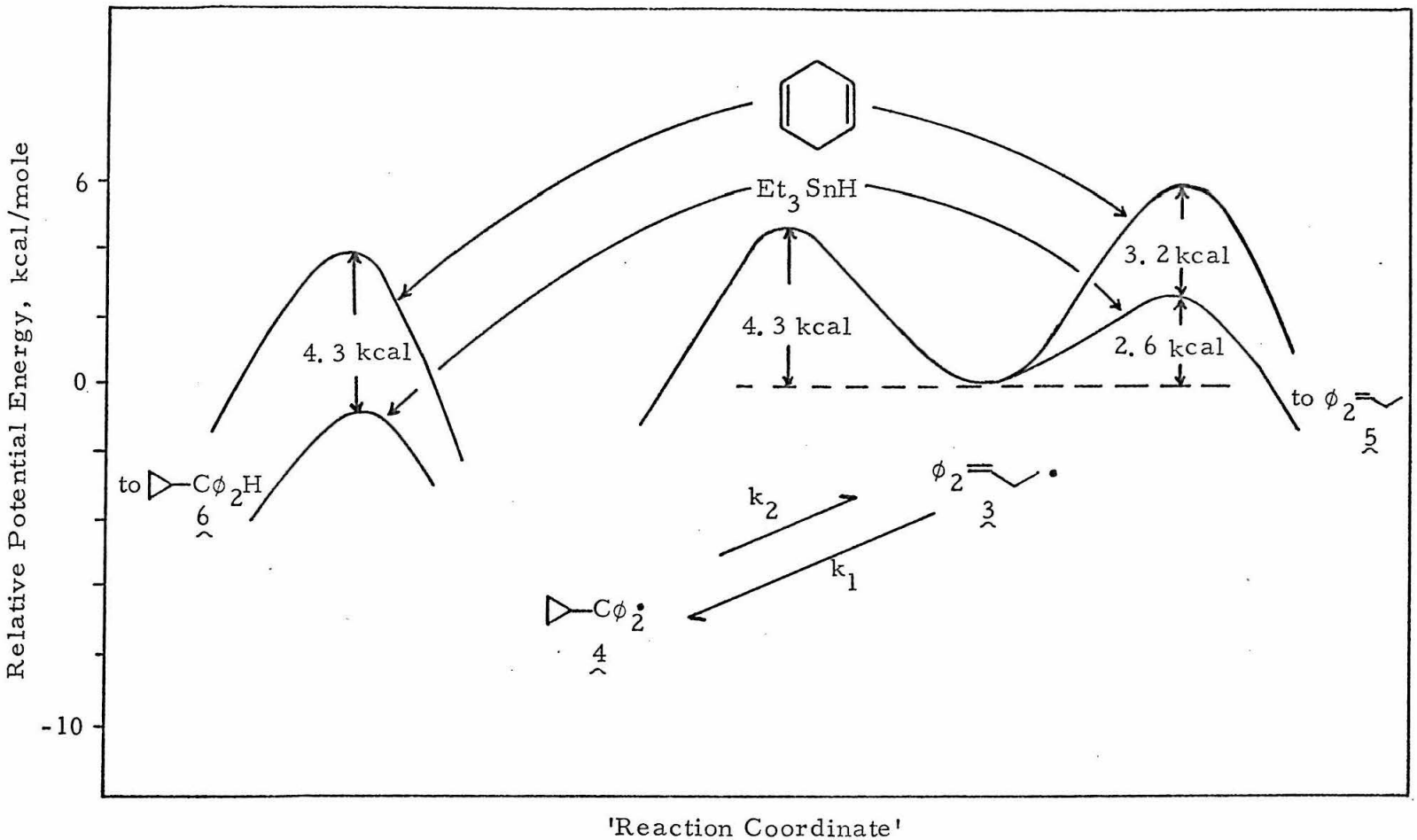
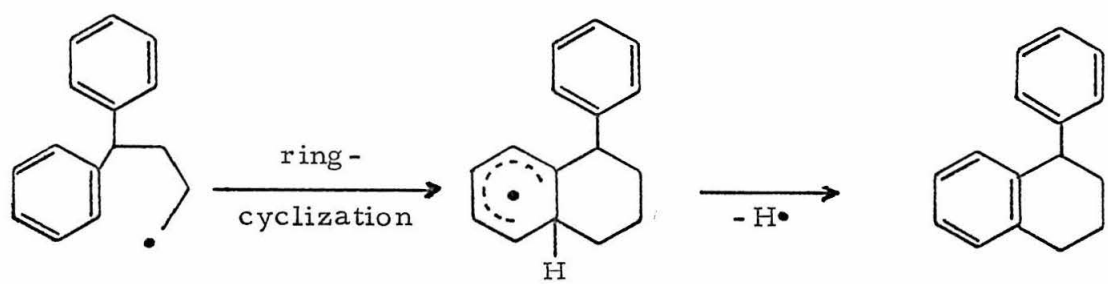


Figure 13. Reaction diagram obtained by superposition of Figs. 10 and 11 according to eq. 1.8-12.

ring-opened perester which involve the double bond should have no counterparts in the decomposition of the so-called saturated perester (8), but others should; thus, comparison of results for the two peresters provides a kind of check on our understanding of the reaction mechanisms and, in particular, on the assessment of the role played by interactions having to do with the double bond.

Results for thermal decomposition of the saturated perester 8 are displayed in Table 3 and immediately following that table in Fig. 3.

Comparison of Figs. 1 and 3 shows that relatively large yields of the unrearranged hydrocarbon, in this case the saturated hydrocarbon 20, are realized and that those yields rise very abruptly with increasing 1,4-cyclohexadiene concentration. The average values, for runs at 152°, of the reduced ratios tabulated in the right-most columns of Tables 1 and 3 are 3.4 and 0.21, respectively. These numbers indicate that the rate of ring-cyclization relative to hydrogen abstraction is greater by a factor of approximately 16 in the unsaturated series.



21 24 25

Of course, consideration of efficiencies for conversion of the ring-cyclized radicals 9 and 24 to the dihydronaphthalene 10 and the tetralin 25 might alter this factor to some degree, but would not upset the

substantial difference which is evident. Possible reasons for a difference of this magnitude will be considered shortly.

The efficiency for conversion of the radical 24 to the tetralin 25 appears to be at most 50%. In particular, for a run at 100° in 3.2 M 1,4-cyclohexadiene in cyclohexane (not shown in Table 3), the peak corresponding to the C of Table 3 was found to be made up of nearly equal areas of a substance tentatively identified as the rearranged hydrocarbon 26 and a second material which might well be a hexahydronaphthalene. The latter would correspond to the tetrahydronaphthalenes

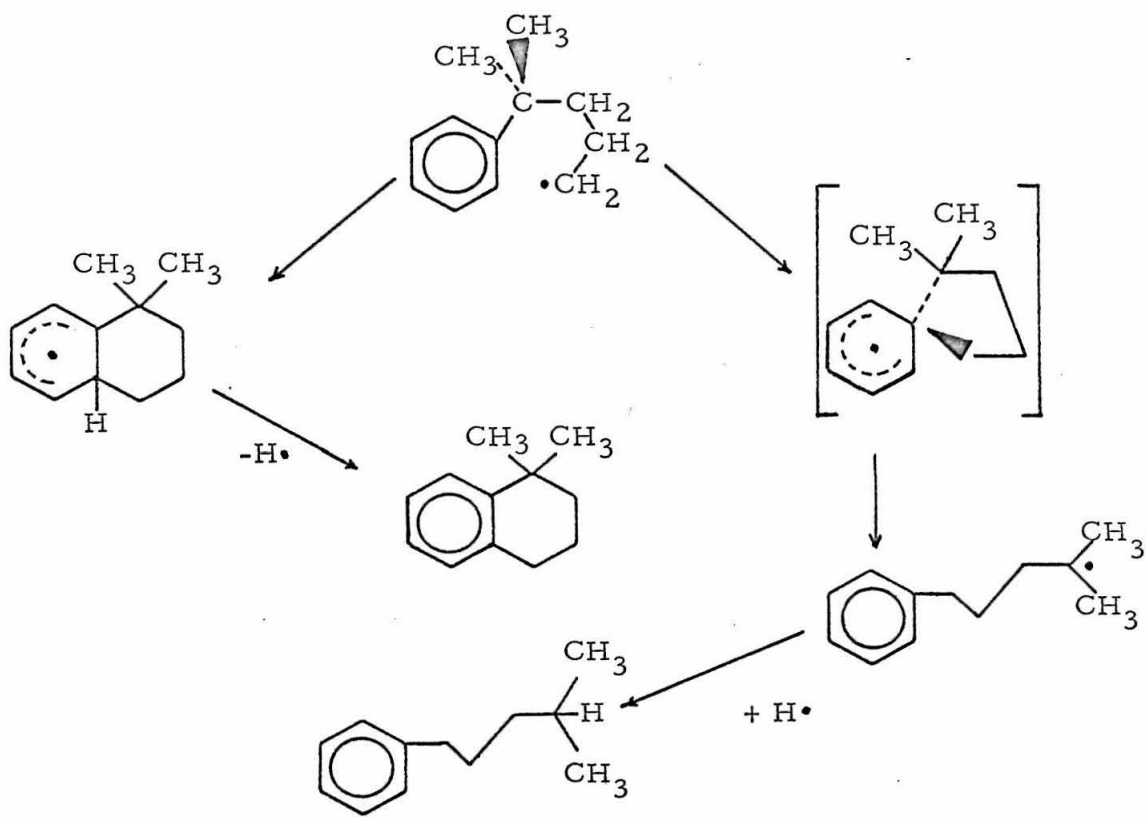
26

implicated in the decomposition of the isomeric ring-opened and ring-closed peresters. As the yield of C is consistently 2--3 times that of the ring-cyclized hydrocarbon 25 when 1,4-cyclohexadiene is present, the yield of 25 evidently therefore accounts for not more than about half of the radicals 24 which are formed.

Identification of the ring-cyclized hydrocarbon 25 and the rearranged hydrocarbon 26 is based on a rather careful investigation of vpc retention times. On Ucon polar, the retention times of C and of 25 agreed within a reasonable experimental error of 2--3 tenths of a percent with those due to authentic 26 and 25. This was true both for the run at 3.2 M cyclohexadiene referred to above and for a run, also at 100°, in neat cyclohexane. On silicone oil, peaks for candidate and authentic 25 again agreed within 2--3 tenths of a percent. However, as noted above, the other peak in the Ucon polar trace was now split into

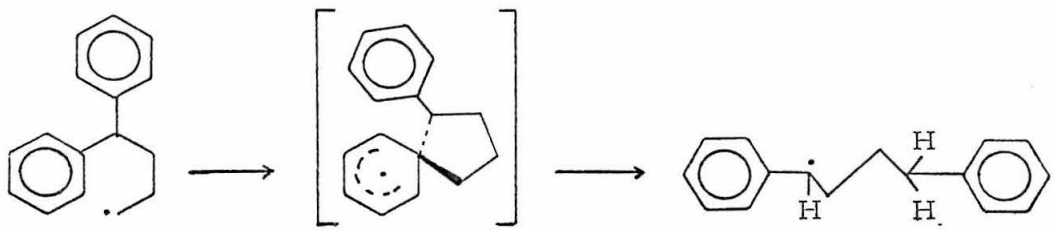
two of about equal intensity in the case of 3. 2 M cyclohexadiene run, one of which again agreed in retention time with authentic 26.

Precedent for formation of 26 can be cited in the work of Winstein and Lapporte (58) who investigated the radical-chain decarbonylation of 5-methyl-5-phenylpentanal (130° in chlorobenzene, initiated by di-t-butyl peroxide). They found that the phenyldimethylbutyl radical shown below cyclized both in the ortho- manner and to the 1-position on the phenyl ring. The ultimate products in the two cases, 1-1-dimethyltetralin and 1-phenyl-4-methylpentane, were detected by infrared in relative amounts of approximately 2. 5:1. A point in question is whether the spiro-radical enclosed in square brackets is a discrete intermediate or merely the transition state for concerted phenyl-group migration.



Even if the former is the case, however, ring-opening to the tertiary radical should be highly favored over reversal to the primary radical. Thus, relative amounts of the two hydrocarbons should broadly reflect the relative rates of the two cyclizations.

In the present system, the analogous five-membered ring spiro radical (27) would also be expected to open to the more stable species, the rearranged radical 28. Assuming that yields of C quoted in Table 3 include hexahydronaphthalene in similar yield to the tetralin 25, relative amounts of 25 and C observed in the presence of 1,4-cyclohexadiene imply that ring-closure of 21 to 24 is favored over



21 27 28

closure to 27 by approximately a factor of 1.5:1. Thus, relative ratios for the two cyclization pathways are similar in this system and in Winstein's.

While combined experimental ambiguities probably disallow quantitative comparison of the partitioning ratios for the two systems, we might note that reliable data on the effect of suitable substituents should indicate whether the phenyl migration is concerted or step-wise; one would expect the ability of the substituent to stabilize a radical center to profoundly influence the rate of the spiro-closure only if the original

carbon-carbon bond is broken as the new bond is formed.

One oddity in Table 3, mentioned briefly above, is that the ratio C:25 is ~2.5:1 in the presence of 1,4-cyclohexadiene, but only 0.2:1 in cyclohexane. This might at first seem inconcistent with our assertion that the spiro-closure product 26 constitutes about half of C for reaction in the presence of cyclohexadiene. The potential problem is that benzylic hydrogens such as those of 26 are no better than comparable in reactivity to cyclohexane towards simple primary radicals or t-butoxy radicals (57, 89). As any 26 formed should therefore not be destroyed under the reaction conditions, the expected facile attack of radicals on the hexahydronaphthalene (which we have said makes up the other half of C in 1,4-cyclohexadiene) might be expected to reduce the ratio C:25 only to ~1. The explanation for the lower ratio actually found in cyclohexane is very possibly that little 26 is formed due to the lack of suitable hydrogen donors for conversion of 28 to 26. While 1,4-cyclohexadiene would be expected to serve admirably, hydrogen abstraction from cyclohexane would be endothermic by approximately 10–15 kcal/mole. Therefore, in cyclohexane 28 may react largely with other radicals, and such reactions could frequently result in coupling rather than formation of 26.

A value of 0.038 was obtained for the ratio 25:20 at 100° for 3.2 M 1,4-cyclohexadiene. Thus the reduced ratio is 0.12 at 100°, about 56% of the average of the values observed at 152°. In obtaining eq. 1.8-6 for k_r/k_a (p. 125), we have tacitly assumed that the efficiency of conversion of the ring-cyclized radical 9 to the dihydronaphthalene 10 is independent of the reaction temperature. On the same

basis, the reduced ratios quoted here indicate that the activation energy for ortho-ring cyclization by the saturated radical 21 exceeds that for hydrogen abstraction from 1,4-cyclohexadiene by 3.5-4 kcal/mole. If we then assume that activation energies for hydrogen abstraction from cyclohexadiene are identical for the radicals 3 and 21, we conclude that the activation energy for ortho-ring cyclization by 21 exceeds that for cyclization by 3 by 2.5—3.0 kcal/mole.

The question now is whether a difference of that magnitude can be rationalized under the assumption that only the classical radicals 3 and 4 need be invoked to account for formation of the isomeric hydrocarbons 5 and 6. This is the question addressed in the major part of the remaining pages of this subsection.

Szwarc and co-workers have carried out abundant experimental determinations of relative rates of addition of methyl radicals to aromatic and olefinic systems (25). Besides finding that strong correlations exist between relative rates of addition for methyl radicals and for ethyl radicals, propyl radicals, trichloromethyl radicals, and styryl radicals, their work is of interest here because relative rates of addition can also be correlated by quasi-theoretical treatments arising from simple Hückel molecular orbital theory (59).

Addition of a radical, anion, or cation to a particular carbon atom of a pi-electron system removes that center from the pi-system. Cyclization by the radicals 3 and 21 are intramolecular examples of such processes. This suggests that rates or activation energies of such addition processes might correlate with the energy necessary to 'localize' the appropriate number of pi-electrons (two for addition of

a cation, one for a radical, and zero for an anion) at the center in question (62). Such a quantity (called the localization energy (61) can be obtained in HMO theory from the pi-electron energies of the initial and the localized systems.

There is some question as to the appropriateness of the localization picture when the resulting intermediate is actually more stable than the separated reactants (as can be shown to be the case for addition of simple alkyl radicals to aromatic systems). Moreover, there is substantial reason to suspect the validity of results obtained by HMO theory. However, the procedure outlined is found to be strikingly successful when applied to Szwarc's data (62, 25). One finds that log (methyl affinity/n), where n is the number of the most reactive positions in the substrate, is linearly related to the radical localization energy, as in Fig. 14 (63).

Leaving aside the question of why so crude a theoretical treatment is successful, the fact that it is, should permit its safe utilization in the problem under consideration. The localization energy for ortho-ring cyclization of the saturated radical 21 is identical in the HMO method to the value (2.54 β) calculated for addition to benzene. For the unsaturated radical 3, however, an ambiguity arises concerning the values employed for the resonance integrals of bonds involving the two olefinic carbons. For aromatic carbon systems, an acceptable procedure (and that employed by Szwarc) is to assign all nearest-neighbor resonance integrals a common value of β, even though the minor variations in bond lengths found experimentally (or approximately predicted by bond orders) might be taken as cause for tying the resonance integral

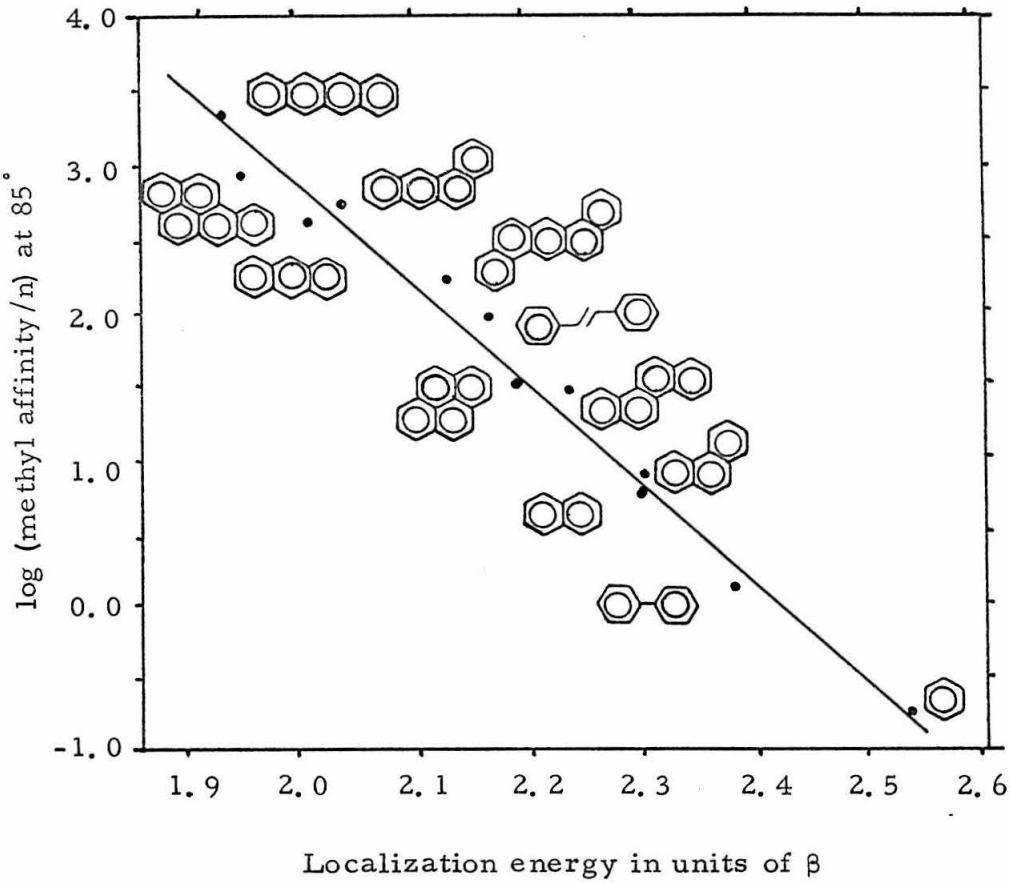


Fig. 14. Correlation of methyl affinities with localization energies.

to the bond length (or to the bond order). For pi-electron systems in which bond lengths range between values close to those expected for classically single and classically double bonds, however, variable values of β must be used (50).

Accordingly, resonance integrals for the three interactions (or bonds) involving the carbon-carbon double bond of the ring-opened radical were obtained by the procedure employed by Szwarc in his

companion study on methyl affinities for olefinic substrates (25). Using trial values of β, the mobile pi-bond orders (73) are calculated, bond lengths are inferred from Coulson's relationship (64), and new values of β corresponding to the calculated bond lengths are assigned from a table given by Roberts and Skinner (65). The cycle is carried to self consistency.* The calculated localization energy is 2.43 β, and the difference in localization energies for the two systems is 0.11 β. (For comparison, use of constant β results in a difference in localization energies of 0.15 β.)

Translation of this difference in localization energies into a difference in activation energies for ring-cyclization requires a further assumption, which we shall take (following the previous investigators) to be that the preexponential factors for addition of methyl radicals to specific centers on aromatic substrates are constant.# From the slope of the straight line in Fig. 14 one then obtains for any two substrates

$$\Delta E_{act} = 11.2\ \Delta L.E. \qquad (1.8\text{-}13)$$

As ethyl affinities and methyl affinities show apparently identical sensitivity to structural variations in the aromatic substrate (25), eq. 1.8-13 should be applicable to such differences in activation energy

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*Final resonance integrals (in units of β for r = 1.393 Å) were 0.86 for the two carbon to phenyl-ring bonds and 1.09 for the carbon-carbon double bond.

#Use of the Arrhenius equation is assumed here. While some positions in polynuclear aromatics 'look' appreciably more hindered than a position in benzene, my experience with many of the systems of Fig. 14 suggests that the positions of minimum localization energy tend to be those which are least stericly congested.

for ortho-ring cyclization by 3 and by 21 as arise from the more extensive pi-system involved in cyclization of the former. The calculated activation energy difference of 1.2 kcal/mole is somewhat less than half the observed value but is at least of the correct sign.

Other factors may of course contribute to the activation energy difference. In particular, there may be specific conformational effects arising from the intramolecular nature of the ring-cyclization. Examination of Dreiding models indeed suggests that the hydrogen atoms on the two methylene groups in 21 may have to become eclipsed in the cyclization. No such unfavorable interaction arises in ring-cyclization by the ring-opened radical 3. A reasonable guess for the extra energy of an eclipsed ethane-like fragment would be 3 kcal/mole, which is the barrier to internal rotation in ethane (90) and is also close to the barriers in many substituted ethanes (90). Thus, a partial eclipsing in cyclization of 21 could well account for the remaining portion of the activation energy difference.

The arguments given above should suffice to show that no contradiction arises, in consideration of activation energies, from the assumption that the classical radicals 3 and 4 account for formation of the isomeric hydrocarbons 5 and 6 as well as for ring-cyclization. We still need to inquire what type of results might signify the intermediacy of a nonclassical radical such as 7. The question is difficult to answer in terms of the activation-energy differences discussed above, but becomes more tractable if relative rates of ring-cyclization and hydrocarbon formation for the saturated and unsaturated systems

are considered. As quoted on page 140, that ratio is greater by a factor of approximately 16 in the unsaturated system.

Let us consider that both the nonclassical radical 7 and the classical radical 3 give rise to ring-opened hydrocarbon 5. In view of the lack of interconversion of cyclobutyl and allylcarbinyl-cyclopropylcarbinyl skeletons in free-radical reactions (see pp. 8, 9), it seems likely that the molecular orbital proscription against a bicyclobutyl-type (p. 8) nonclassical free radical in favor of a homoallyltic structure (such as 7) is valid (13). For geometrical reasons, then, we can assume that only the classical radical 3 undergoes the ring-cyclization. It follows that formation of substantial amounts of ring-opened hydrocarbon from the nonclassical radical 7 should lead to a rate of ring-cyclization relative to hydrocarbon formation which is anomalously low by comparison to the saturated model.

The question, then, is whether the factor of 16 is 'anomalously low'. As discussed above in terms of activation energies, the more extensive pi-system in the unsaturated system should favor ring-cyclization by 3 over ring-cyclization by 21. The 1.2 kcal/mole inferred from the localization energies is equivalent, at 152°, to approximately a factor of 4. This leaves a factor of 4 to be accounted for in other ways. In 21, the radical center can cyclize to either of two phenyl rings, while in 3, the geometry about the double-bond renders only one of the rings accessible. However, this factor may be more than offset by the existence of the additional carbon-carbon single bond in 21, which would seem to allow the radical center of 21 to explore

many more regions of space quite remote from the phenyl rings than are permitted the ring-opened radical 3.

Additional factors are the eclipsing which may be required for ring-cyclization by 21 and, according to Dreiding models, the greater distance of minimum approach (without stretching bonds) between radical center and ortho-carbon in the unsaturated series.

Clearly, a quantitative assessment of all the relevant factors is quite impossible. Still, it is possible to say that there is no compelling reason to suspect that a mechanistic formulation involving only classical radicals is defective. On balance, this constitutes yet another occasion in which a nonclassical radical, if it exists, might have made its presence felt, but failed to do so.

Consideration of localization energies is useful in answering the potentially troubling question of whether 3 might be able to undergo a spiro-closure similar to that inferred for 21. The problem is that the assumption that B is comprised of isomeric tetrahydronaphthalenes is crucial to the estimation of efficiencies of conversion of 9 to 10, and thus to the indirect comparison we have made through eqs. 1.8-6 and 1.8-11 of relative rates of attack of 3 on 1,4-cyclohexadiene and triethyltin hydride. To show that spiro-closure by 3 is not an attractive process, we have calculated the localization energy for that process. The result, 2.82 β is 0.39 β higher than that for ortho-ring cyclization. According to eq. 1.8-13, this difference is equivalent to an activation energy difference of 4.4 kcal/mole, which in turn implies a rate difference of ~ 350 at 100°. As spiro-closure and ring-cyclization by 21 occur at comparable rates, and as the localization energies for the two

processes are identical in the HMO method, the implication is that ring-cyclization by 3 should be favored over spiro-closure by a factor of ~350.

The same conclusion can perhaps be reached less esoterically by noting that 3 is a much more stable radical than the vinylic radical which would result from the alternative opening of the unsaturated analog of spiro radical 27.

9. Radical-induced Decomposition in Triethyltin Hydride

In the preliminary discussion in subsection 5A, we noted that under certain assumptions (survival of the cage ether; no interdiction of cage processes via rapid abstraction of hydrogen from triethyltin hydride by any of the caged species), the fraction of normal decomposition of perester 1 in triethyltin hydride is given by the ratio of the yield of cage ether 12 to that which would be observed in the absence of induced decomposition. As we have no way of suspending the radical-induced decomposition at the relatively high (ca. 1 M) triethyltin hydride concentrations where radical-induced decomposition predominates, we can not of course know with absolute certainty what the efficiency of production of the ether 12 would be under those circumstances: and either the physical or the chemical properties of the tin hydride could, in principal, occasion a substantial drift in the yield of 12 with the hydride concentration, even if no question of radical-induced decomposition arose.

It was also shown in subsection 5A that physical properties of the

solvent can markedly affect the efficiency of cage ether formation. In particular, the so-called kinematic viscosity--the ratio of viscosity to specific gravity--seemed to be a useable measure of the ability of a solvent to keep the caged particles long confined, and thus to promote cage recombination or other cage reaction. At 20° the viscosity and kinematic viscosity of n-octane are 0.54 and 0.78, respectively (91). The analogous quantities are not known for triethyltin hydride, but I have investigated tetraethyltin; its viscosity at 20° is 0.63, its specific gravity is reported to be 1.19 (92), and thus its kinematic viscosity is 0.53. The figures for triethyltin hydride are expected to be rather similar. As the highest tin hydride concentration investigated (0.94 M) is still 80% n-octane by volume, the kinematic viscosity of the solution is not likely to differ substantially from that of n-octane itself. Thus, competition between cage recombination and diffusive separation of the caged particles may safely be taken to be substantially independent of tin hydride concentration for the relatively dilute solutions investigated in this work.

The chemical properties of triethyltin hydride are cause for somewhat greater concern. Specifically, hydrogen abstraction from triethyltin hydride by t-butoxy radical might compete with cage recombination and with diffusion from the solvent cage, at least at the higher tin hydride concentrations. That hydrogen abstraction reaction is expected to be exothermic by roughly 40 kcal/mole. Moreover, attractive polar contributing structures can be written for the transition state in question. These considerations suggest a reaction of low activation energy, if it is not actually diffusion-controlled. Moreover,

scavenging of precursor acyloxy radicals by the tin hydride could in principle also affect the yield of the ether 12. However, this possibility can be discounted on the basis of the study reported by Neumann, Rubsamen, and Sommer on radical-induced decomposition of diacylperoxides in triethyl- and tri-n-butyltin hydride (93). They found that 0.5—1 M tin hydride efficiently traps relatively stable benzoyloxy radicals, but that even at room temperature decarboxylation of acetoxy and lauryloxy radicals ($CH_3(CH_2)_{10}CO_2\cdot$) is more than competitive with hydrogen abstraction from the tin hydride. Their results suggest that at the much higher temperatures employed in this work, scavenging of simple acyloxy radicals should be negligible.

In any case, evidence to be presented shortly strongly suggests that the yield of ring-opened ether 12 is not measureably affected by scavenging of caged radicals by triethyltin hydride.

Thus, the major source of uncertainty in any conclusions drawn from observed yields of the ether 12 would appear to arise from error in the measurements of the ether yields. The yield of 12 for 100% normal homolytic decomposition in n-octane solution can be inferred from the run shown in row 5 of Table 8. As previously noted, 0.2 M 1,4-cyclohexadiene (2% by volume) was employed in that run to moderate the reaction and thus to insure the survival of the cage ether. The fact that a rather normal 1.4% yield of the sensitive butadiene 13 survives the decomposition confirms the efficacy of the small cyclohexadiene concentration employed. Thus, the expected yield of 12 for 100% normal decomposition (hereafter abbreviated 100% n) at 110° is 12%. A reasonable estimate of the uncertainty in this value is ± 1%. As the

viscosity of the reaction mixture will be somewhat less at 125° than at 110°, the yield of 12 is expected to be slightly less, as is in fact observed (Table 1) for decomposition of 1 in cyclohexane-cyclohexadiene mixtures. We shall adopt a value of 11 ± 1% for use at 125°. The principal uncertainty, however, is that in the determination of the ether yields for the decompositions in the presence of the tin hydride. For the four runs at 125° from 0.044 to 0.94 M triethyltin hydride, 1-phenylnaphthalene, which has a retention time about 10% less than that for the ether 12 (Ucon polar), was used as the internal standard in relatively large amounts. As a result, the ether appears as a relatively small peak on the tail of the 1-phenylnaphthalene, and those yields are probably good to not better than ± 20% relative. In contrast, the two 0.01 M tin hydride runs were subsequently carried out with extraction of the ether yields as the primary goal, and those ether yields should be good to ± 5%.

Percents of normal decomposition and standard errors calculated by propagation of errors from the quoted uncertainties in the ether yields are given in column 5 of Table 15 (p. 172). The sixth column of that table contains the fractions of normal decomposition calculated in a second way--from reaction rates measured at 110°. The numbers quoted are derived from ratios of rate constants for perester disappearance taken with respect to Howden's value of 0.0046 min^{-1} for chlorobenzene solution at 110° (see eq. 1.9-2).

Actually, the derived rate constants (see Figs. 15-18) were not obtained by following the decreasing perester concentration with time, but rather by following the increasing concentration of tin ester 14;

the former course of action is rendered impractical (for triethyltin hydride--perester concentration ratios larger than about 5) by the strong, broad absorbance (Sn - H stretching) of the tin hydride at 1813 cm^{-1} which obscures the only strong perester absorbance, the carbonyl band at about 1785 cm^{-1}.

Figs. 15-18 are plots of absorbance of tin ester at the carbonyl maximum of 1651 cm^{-1} against time for degassed thermal decomposition. The perester disappears with a total rate constant, k_T, which is related to the rate constant for normal decomposition, k_o, according to eq. 1.8-1, where the concentration of perester 1 is denoted by (P), of triethyltin radicals by (Sn·), and the rate constant for attack of Sn· on P is denoted by k_1.

$$-d(P)/dt = k_o(P) + k_1(Sn\cdot)(P) = k_T(P) \quad . \qquad (1.9\text{-}1)$$

The fraction of induced decomposition is given by

$$k_o/k_T = (1 + k_1(Sn\cdot)/k_o)^{-1} \quad . \qquad (1.9\text{-}2)$$

Because the induced decomposition is very nearly first order in perester,* the tin ester absorbance, which is proportional to the tin ester concentration, is proportional to the concentration of perester which has undergone decomposition. As such, the rate constant extracted from the dependence of absorption on time is k_T. The equation (A(t) is absorbance at time t; A_o, at t = 0; and A_∞, at t = ∞)

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*This statement will be justified later in this subsection. Perhaps we should point out that this fact justifies our taking k_T to be constant in the treatment of the kinetic data given here.

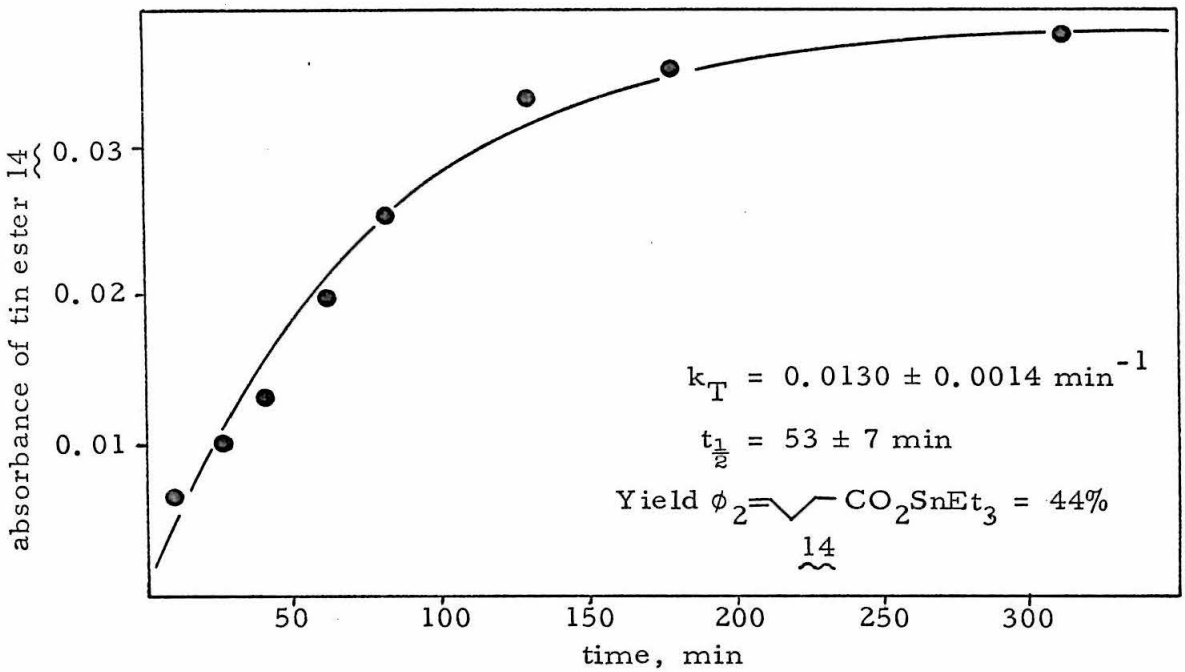


Figure 15. Decomposition of 0.002 M t-butyl (γ, γ-diphenylallyl)peracetate in 0.010 M triethyltin hydride in n-octane at 110°; not shown is a measurement at 550 min, absorbance = 0.0373.

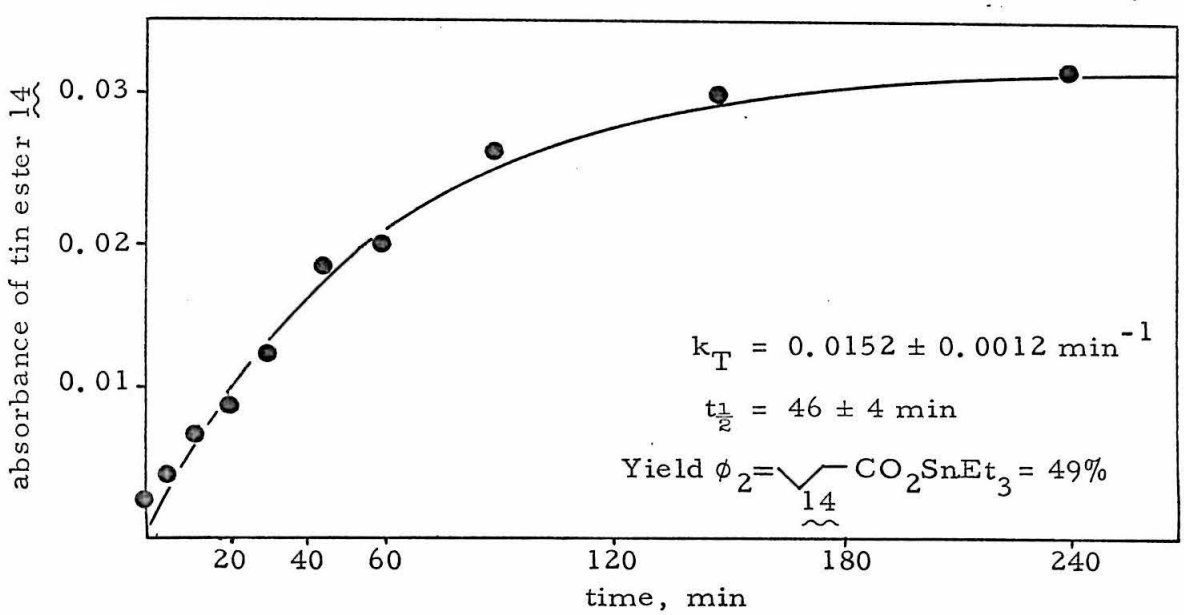


Figure 16. Decomposition of 0.002 M t-butyl (γ, γ-diphenylallyl)peracetate in 0.044 M triethyltin hydride in n-octane at 110°.

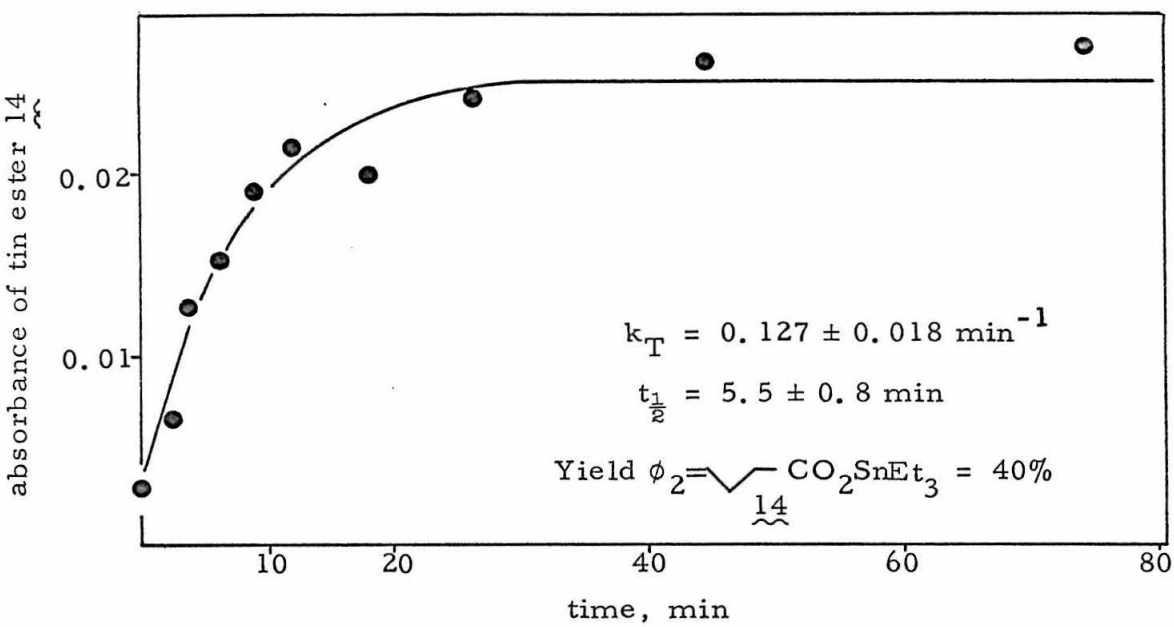


Figure 17. Decomposition of 0.002 M t-butyl (γ, γ-diphenylallyl)peracetate in 0.41 M triethyltin hydride in n-octane at 110°.

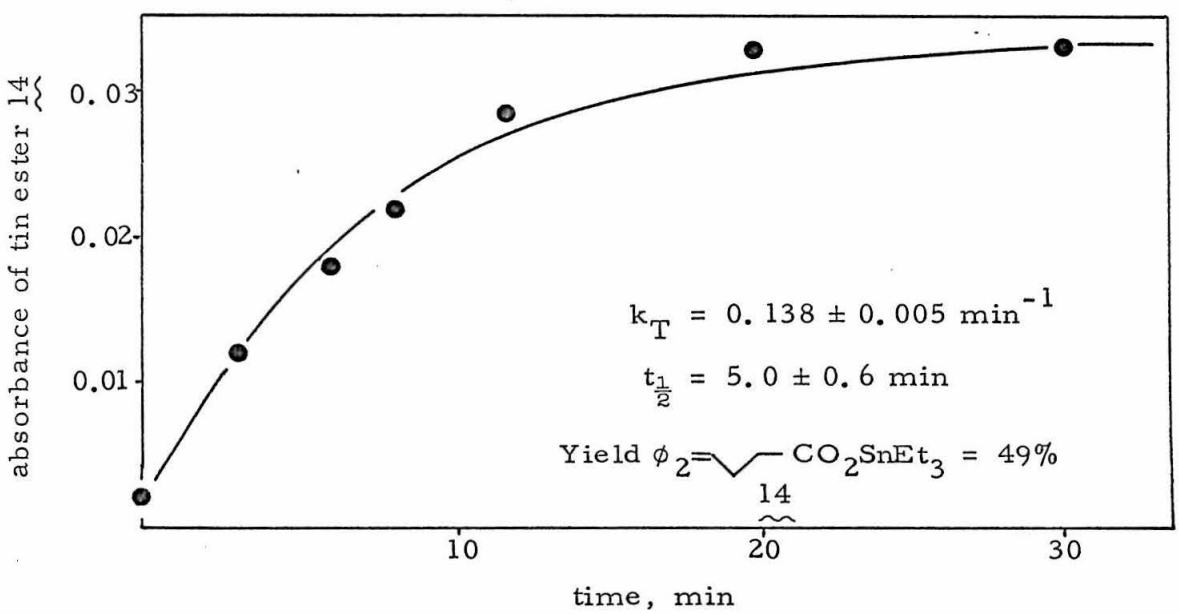


Figure 18. Decomposition of 0.02 M t-butyl (γ, γ-diphenylallyl)peracetate in 0.67 M triethyltin hydride in n-octane at 110°; not shown is a measurement at 112 min, absorbance = 0.0313.

$$A(t) = A_\infty - (A_\infty - A_o) \exp(-k_T t) \qquad (1.9\text{-}3)$$

is obtained. Rearranging and taking logarithms gives the more commonly used logarithm form:

$$\ln (A_\infty - A(t))/(A_\infty - A_o) = -k_T t \qquad (1.9\text{-}4)$$

The absorbance data have not been exhibited in logarithmic form, as is usually done, however, because the nature of the experimental errors would make such a treatment highly misleading with the present data. The principal error, that in the absorbance reading, is expected to be fairly constant (and of substantial magnitude) throughout the run. For relatively long times, when A(t) approaches A_∞, the relative error in $A_\infty - A(t)$ can become very large. As a result, a linear plot according to eq. 1.9-4 would have to feature error brackets which increase enormously at long times to keep in perspective the significance of deviations from the line. Under these circumstances, it seems better to plot absorbance vs. time, where deviations from the calculated least-squares lines are expected to be independent of time.

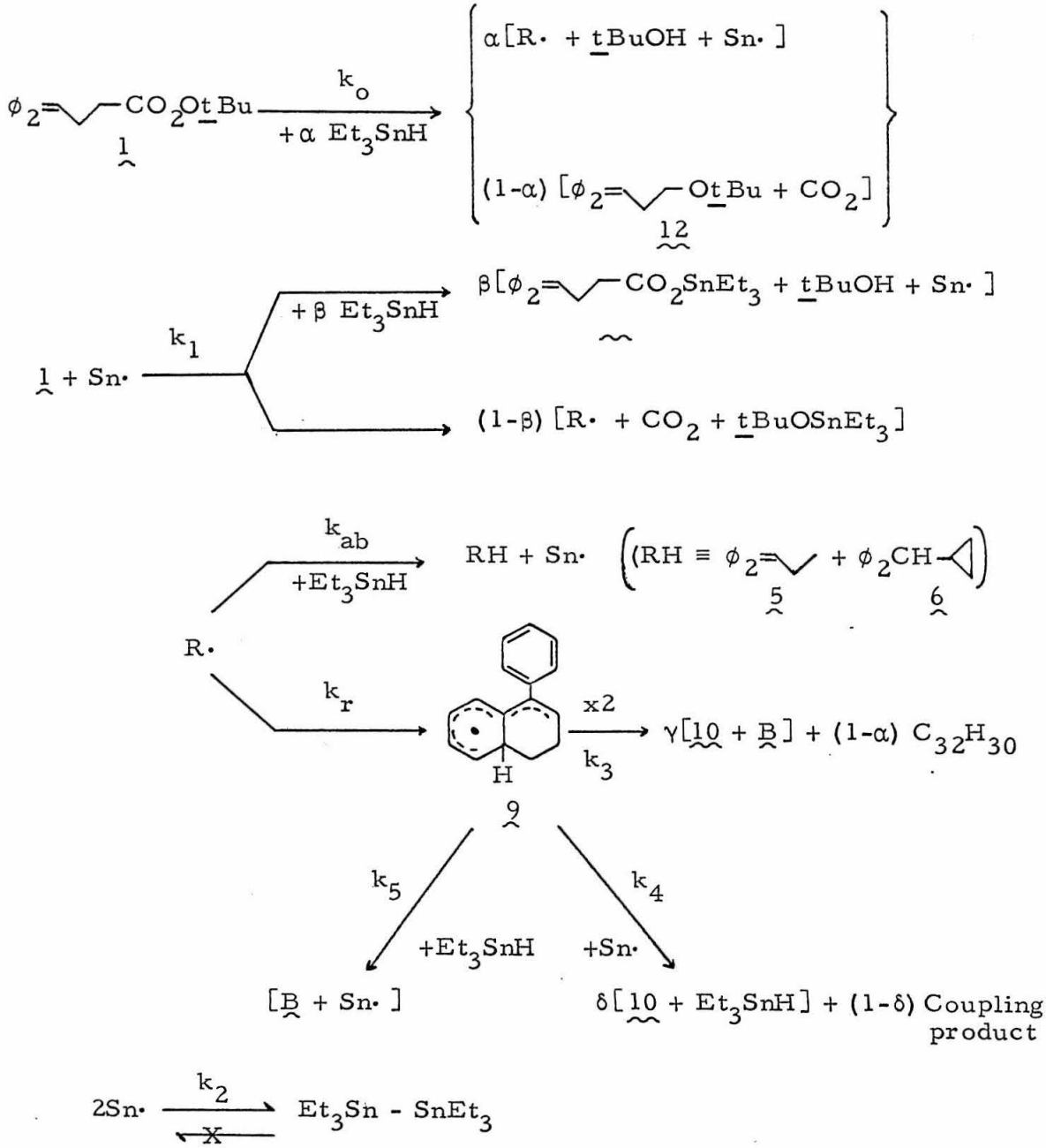
Extraction of rate constants and standard deviations was carried out using the formalism put forth in Section Two. Incidentally, a particular advantage of that formalism is that the results are independent of which form of a relationship (e.g., eq. 1.9-3 or eq. 1.9-4) is used (76).

Examination of Figs. 15-18 indicates a generally satisfactory fit to the lines drawn. The obviously sizable experimental errors in the absorbance measurements arise from the necessity of using extreme

conditions (1-mm path length, 90 to 100% transmission range on a Beckman IR-7) in order to investigate initial perester concentrations (about 0.002 M) similar to those which previously had been employed in the product studies. Lack of any significant systematic errors (early points low, later points high, or vice-versa) would seem to confirm the applicability of first-order kinetics.

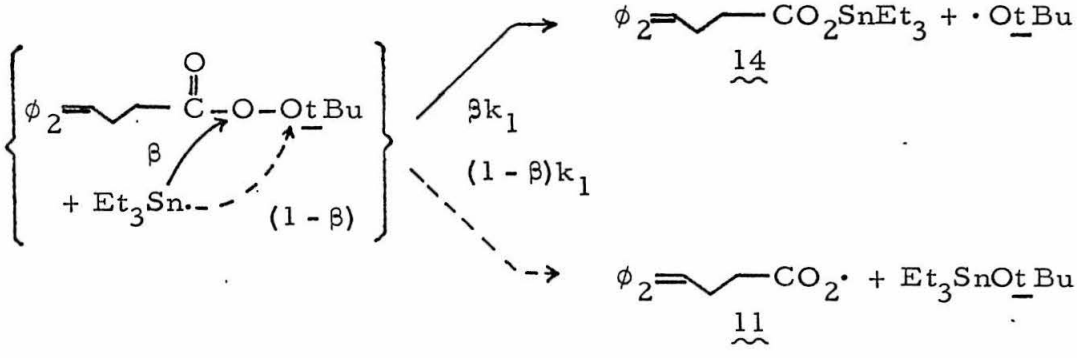
The real evidence that the induced decomposition is essentially first order in perester comes, however, from calculations based on the reaction stoichiometry. In this, the third approach, for calculating the balance between normal homolytic and radical-induced decomposition, we shall derive an expression for (Sn·) for substitution into eq. 1.9-2. As mentioned previously, inefficiency in the replacement of the triethyltin radical consumed in induced decomposition constitutes a mechanism for chain termination. The reaction steps we shall consider are depicted in Chart 5. Brackets which appear in the chart confine products which are produced together in particular reaction steps. The normal perester decomposition produces cage ether and carbon dioxide with an efficiency of $(1 - \alpha) = 0.13$ at 110°, and a pair of radicals with an efficiency of α. (The symbol R· represents both ring-opened and ring-closed radicals in a general sense as explained below.) I have written the species produced along with R· as t-butyl alcohol and a triethyltin radical; under the assumption that the t-butoxy radical invariably and rapidly abstracts hydrogen from triethyltin hydride, that formulation is kineticly equivalent, within the framework of steady-state kinetics, to presenting the t-butoxy radical as a discrete intermediate. The coupling of t-butyl alcohol and triethyltin radical in the

Chart 5. Mechanistic Scheme for Radical-Induced Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate in Triethyltin Hydride.



following line is similarly motivated. That reaction--actually, it is shown as the upper branch of two--represents radical-induced decomposition involving attack of a triethyltin radical on the carbonyl peroxy oxygen of the ring-opened perester. We shall let β stand for the probability that the radical-induced decomposition takes this pathway. The tin radical might also attack the ether peroxy oxygen, as shown in Chart 6. The probability that induced decomposition will take the latter course is then 1 - β.*

Chart 6. Radical-Induced Decomposition of t-Butyl (γ, γ-Diphenylallyl)-peracetate by Triethyltin Radical.



The formulation depicted in Chart 5 is meant to draw attention to the different mechanistic consequences of the two modes of induced decomposition: in the ester-forming reaction, replacement of the attacking triethyltin radical is virtually guaranteed, whereas, if the tin

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*A third possibility--attack by tin radical on the doubly-bonded carbonyl oxygen itself--can probably be excluded on the basis of the report (77) that the triethyltin radical attacks benzoyl peroxide, to within experimental error, only at peroxy oxygen and not at carbonyl oxygen.

ether* is formed, the probability of replacement of the tin radical depends on a number of factors. The radical R· may abstract hydrogen from the tin hydride, but may undergo ring-cyclization, whence replacement of the tin radical becomes doubtful. Three ways in which ring-cyclized radicals may be consumed are shown in Chart 4. To the right is depicted the reaction of a pair of ring-cyclized radicals to form the dihydronaphthalene 10. The conversion efficiency for this reaction must of necessity be less than or equal to 50% (i.e., $\gamma \leq 1$). Next we have transfer of a hydrogen atom from a ring-cyclized radical to a triethyltin radical or coupling of the two radicals. Finally, hydrogen abstraction by ring-cyclized radical from the tin hydride is the only one of the three conversion reactions which enables the chain to be propagated. Not considered is the possibility of reversal of the ring-cyclization. Its inclusion would greatly complicate the kinetic analysis. Fortunately, the evidence that little or no decyclization occurs in 1,4-cyclohexadiene, even at 0.001 M ring-opened perester (pp. 114, 115, 287-290) justifies its neglect here. Significant hydrogen abstraction by ring-cyclized radicals from solvent was not observed in

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*Direct evidence for formation of t-butoxytriethyltin has neither been obtained nor seriously pursued. However, formation of tin ester in yields of only about 50% where other evidence (see Table 15) points to nearly exclusive radical-induced decomposition leaves little room for doubt as to the existence of two modes for the induced decomposition. Kuivila cites a personal communication from Sawyer to the effect that trialkylalkoxytin compounds react with excess tin hydride to yield the alcohol plus the hexaalkylditin (80). Thus, the tin ether may well not survive the reaction. This would be of interest for our purposes only if reaction of the tin ether with the tin hydride were to involve free-radical intermediates; and this is not known, although it is Kuivila's guess that free-radical intermediates are not involved (81).

1,4-cyclohexadiene (it would have lead to symptoms of the same type expected for decyclization), but as triethyltin hydride has been shown to be a much more active hydrogen donor than 1,4-cyclohexadiene (p. 132), the possibility can not be excluded here.

We can now give a kinetic treatment which will serve to illustrate several main features. This treatment will leave open the precise connection between a certain probability function g and the rate constants for reactions of ring-cyclized radicals; that connection will be developed in Appendix A and simply referenced here. The reason for the adoption of this seemingly round-about procedure is that giving the complete analysis here would be less instructive and would seriously risk hopelessly entangling the discussion in mere algebraic manipulation.

From eqs. 1.9-1 and 1.9-2, we see that prediction of the fraction of induced decomposition requires the development of an expression for $k_1(Sn\cdot)/k_o$. We proceed by writing down (in somewhat novel form) the rate law for (Sn·):

$$d(Sn\cdot)/dt = \alpha k_o(P)f + \alpha k_o(P) - k_1(Sn\cdot)(P) + \beta k_1(Sn\cdot)(P) + (1-\beta)k_1(Sn\cdot)(P)f - 2k_2(Sn\cdot)^2 \quad (1.9\text{-}5)$$

The function f which appears in the above is defined to be the probability that a tin radical will be generated as a radical R· is rapidly converted to product; if ring-cyclization did not occur, and R· invariably abstracted hydrogen from triethyltin hydride, f would be 1.*

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*Perhaps the term 'probability' is inappropriate, for the range of f is not 0 to 1, but -1 to 1: if all radicals R· ring-cyclize and are subsequently converted to product by consuming a triethyltin radical, f would be -1.

Thus, the first term on the right-hand side represents the rate of formation of tin radicals, through the intermediacy of R·, due to normal decomposition of the perester. The second term describes the formation of the tin radical shown in the top line of Chart 5. The third term describes the consumption of tin radicals in the induced decomposition. The fourth indicates the 'immediate' replacement of a tin radical for that fraction, β, of the induced decompositions which give tin ester. The fifth is motivated similarly to the first: it describes the rate at which tin radicals are generated via induced decomposition giving tin ether and a hydrocarbon radical. The last term describes pairwise destruction of tin radicals.

The usual procedure, invoking the steady-state approximation $d(Sn\cdot)/dt = 0$, will allow us to solve for the Sn· concentration. Before doing so, it is interesting to note what would happen if f were equal to 1: the second, third, and fourth terms would add out, giving

$$(Sn\cdot) = [\alpha k_o (P)/k_2]^{\frac{1}{2}} \quad . \qquad (1.9\text{-}6)$$

Then, according to eq. 1.9-1, the induced decomposition would be 3/2 order in perester. However, because f must be less than 1 to account for formation of the dihydronaphthalene 10, the three terms can not add out, but when summed are--like the last term--negative. This provides an alternative mechanism for chain termination. Thus, reaction of pairs of triethytin radicals can be negligible even though there be no cosmological prohibition against such reaction.

Termination by coupling of triethyltin radicals should be more

important the closer f is unity, which means the higher is the triethyltin hydride concentration. For a 3/2 order induced decomposition under conditions where little normal decomposition occurs, the rate 'constant' k_T would then go as the square root of the perester concentration. The first-order kinetic analyses described earlier gave $k_T = 0.127\ min^{-1}$ for 0.002 M perester in 0.4 M tin hydride at 110° (see Fig. 17). If the induced decomposition were really 3/2 order, data for the same hydride concentration and reaction temperature, but for 0.02 M perester also erroneously treated by first-order kinetics would give an apparent k_T about $\sqrt{10} \cong 3$ times larger. This particular experiment was not carried out, but we do have one for 0.02 M perester and 0.67 M hydride (see Fig. 18). Because the higher tin hydride concentration should lead to more efficient chain propagation (if it had any effect), the 'first-order' rate constant for that run would be more than three times that for the run of Fig. 17 if induced decomposition were 3/2 order. Instead, the value found, $0.138\ min^{-1}$, is only about 10% greater. It is in larger part this comparison which disallows significant pairwise reaction of tin radicals for any reaction conditions considered. Thus, the k_2 reaction may be dropped from the reaction scheme. Incidentally, neglect of the back reaction (see Chart 5) is based on experimental evidence which demonstrates that hexaalkylditins do not dissociate at temperatures under 200° (78).

Setting $d(Sn\cdot)/dt = 0$ after dropping the last term in eq. 1.9-5 gives the expression we have been seeking:

$$\frac{k_1(Sn\cdot)}{k_o} = \frac{\alpha}{(1-\beta)} \frac{(1+f)}{(1-f)} \quad . \qquad (1.9\text{-}7)$$

The probability function f can be expressed as the sum of two probabilities:

$$f = f_1 + (1 - f_1)g \quad . \qquad (1.9\text{-}8)$$

The symbol f_1 in eq. 1.9-8 denotes the probability that R· abstracts hydrogen from triethyltin hydride. Therefore, $1 - f_1$ is the probability that ring-cyclization occurs. Finally, g stands for the probability that conversion of a ring-cyclized radical $\underset{\sim}{9}$ to product will occur so as to generate a triethyltin radical. Of course, conversion of $\underset{\sim}{9}$ to product might also consume a tin radical; if this were invariably to happen, we would have $g = -1$.

By the definitions given above, f_1 is simply the rate of formation of ring-opened plus ring-closed hydrocarbon divided by the sum of those rates plus the rate at which ring-cyclization proceeds. Using rate constants previously defined (pp. 92, 110),

$$f_1 = \frac{k_a(\phi_2\text{=}\!\!\sim\!\!\cdot)(Et_3SnH) + k_b(\triangleright\!\!-C\phi_2\cdot)(Et_3SnH)}{k_a(\phi_2\text{=}\!\!\sim\!\!\cdot)(Et_3SnH) + k_b(\triangleright\!\!-C\phi_2\cdot)(Et_3SnH) + k_r(\phi_2\text{=}\!\!\sim\!\!\cdot)} \qquad (1.9\text{-}9)$$

Because the ring-opened and ring-closed radicals rapidly equilibrate at temperatures employed for decomposition of the ring-opened perester (subsection 7, pp. 90-97), the concentration of ring-closed radical can be replaced by that of the ring-opened radical times the equilibrium constant k_1/k_2. This allows the cancellation of the radical concentrations in eq. 1.9-9. With the definition

$$k_{ab} = k_a + (k_1/k_2)k_b = k_a(1 + k_1k_b/k_ak_2) \quad , \qquad (1.9\text{-}10)$$

eq. 1.9-9 can be rewritten as

$$f_1 = k_{ab}(Et_3SnH)/(k_{ab}(Et_3SnH) + k_r) \quad .$$

The ratio k_1k_b/k_ak_2 will be recognized (p. 93) as defining the characteristic ratio for hydrogen abstraction from triethyltin hydride. Its value is about 0.07 at 110 or 125°. Thus, $k_{ab} = 1.07\ k_a$, and (no longer suppressing the superscript SnH on k_a) we have

$$f_1 = 1.07(k_a^{SnH}/k_r)(Et_3SnH)/\left[1.07(k_a^{SnH}/k_r)(Et_3SnH) + 1\right] \quad (1.9\text{-}11)$$

It should be clear from subsection 8 that any uncertainty in the factor of 1.07 will be dwarfed by that in k_a^{SnH}/k_r.

Substituting eq. 1.9-11 into eq. 1.9-8 and substituting the result into eq. 1.9-3 gives eq. 1.9-12.

$$\frac{k_T}{k_o} = 1 + \frac{k_1(Sn\cdot)}{k_o}$$

$$= 1 + \frac{\alpha}{1-\beta}\left\{\left(\frac{2}{1-g}\right)(1.07\ k_a^{SnH}/k_r)(Et_3SnH) + \frac{1+g}{1-g}\right\} \quad . \qquad (1.9\text{-}12)$$

The percent of normal decomposition (% n) is simply given by 100 times the reciprocal of eq. 1.9-12.

Because the function g is undefined except in a general sense, eq. 1.9-12 is only of limited usefulness. Nonetheless, certain limiting cases can be treated. As noted above, we could force g to be +1 under all reaction conditions studied by selecting a sufficiently large value for k_5 (see Chart 5). However, the fact that dihydronaphthalene is always

observed means that g must always be less than 1. This is just as well, for eq. 1.9-12 is singular for g = 1. This result of course arises from our earlier neglect of the pairwise reaction of triethyltin radicals, the alternative mechanism for chain termination.

An interesting special case is g = 0; this can be arranged by agreeing to let ring-cyclized radicals react only with each other. Indeed, this was the basis on which the expression for k_r/k_a^{SnH} (eq. 1.8-11) was evaluated. Setting g = 0 in eq. 1.9-12, and using eq. 1.8-11, gives

$$\% \; n = 100 \left[1 + \frac{\alpha}{1-\beta} \left\{ 0.028 \exp(4.3/RT)(Et_3SnH) + 1 \right\} \right]^{-1}. \quad (1.9\text{-}13)$$

Provided that α and β can be evaluated, eq. 1.9-13 is nice, clean, and readily testable. The parameter α is simply (1 - the cage efficiency), or 0.87 at 110° and 0.88 at 125°. β is the fraction of induced decompositions yielding the tin ester; its value is somewhat uncertain, but is clearly close to 0.5, as can be seen from yields of tin ester reported in Table 10. One puzzling fact must be admitted here: since the percent of induced decomposition increases with increasing tin hydride concentration, one would expect the yield of the tin ester to be greater at the higher tin hydride concentrations. However, the trend in Table 10 is, if anything, in the opposite direction. Perhaps this is partly due to experimental error of the same sort which lead to relatively large standard deviations in the rate constants for the kinetic measurements at 110° (from which the yields of tin ester were also calculated). The value $\beta = 0.55$ (which blames

deviations about equally on all the experimental determinations) will be used.

Calculation 1 of Table 15 lists values of % n given by eq. 1.9-13.*

The special case g = -1 can be arranged by postulating a sufficiently high value for the rate constant for reaction of a ring-cyclized radical with a triethyltin radical. Equation 1.9-12 then leads to

$$\% \, n = 100 \left[1 + \frac{\alpha}{1-\beta} \left\{ 1.07 \, k_a^{SnH} (Et_3SnH)/k_r \right\} \right]^{-1} . \quad (1.9\text{-}14)$$

For this case, the conversion of ring-cyclized radicals to the dihydronaphthalene could be much more efficient than was previously assumed in deriving eq. 1.8-11 for k_r/k_a^{SnH}. We can put the efficiency at 100%** by dividing eq. 1.8-11 by a factor of 0.325 = 0.5 γ. Then eq. 1.9-14 becomes

$$\% \, n = 100 \left[1 + \frac{\alpha}{1-\beta} \left\{ 0.086 \exp(+4.3/RT)(Et_3SnH) \right\} \right]^{-1} . \quad (1.9\text{-}15)$$

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*Actually, values of k_a^{SnH}/k_r employed at 110 and 125° were chosen in all calculations listed in Table 15 to exactly reproduce the reduced ratios R (see eq. 1.9-19) obtained experimentally in the 0.011 M triethyltin hydride run at each temperature. If the two central points in Fig. 12 (p. 137) lay precisely on the best fit line, these values would be identical to those contained in eqs. 1.9-13 and 1.9-15.

Error limits in the 10 calculations listed in Table 15 were calculated according to eq. 2.2-19 (p. 218) assuming the following standard errors in the various parameters: 0.02 for α; 0.03 for β; and 20% of value for k_a^{SnH}/k_r. The latter uncertainty arises from that in the assumed conversion efficiency as well as experimental uncertainty in the values of the reduced ratio R to which values of k_a^{SnH}/k_r have been fit.

**This corresponds to putting δ (Chart 5) = 1.0 and assuming that ring-cyclized radicals react solely with triethyltin radicals.

Values calculated from eq. 1.9-15 are given as Calculation 2 of Table 15.

We can now examine the agreement of the g = 0 and g = -1 mechanistic treatments with predictions from yields of the cage ether 12 and reaction rates recorded in columns five and six of Table 15. With the exception of the 110° run at 0.002 M perester and 0.4 M tin hydride, the g = 0 predictions agree rather well with those from ether yields and reaction rates. The similar amounts of normal decomposition at 0.01 and 0.04 M tin hydride indicated both by the ether yield and reaction-rate criteria arises naturally for g = 0: if induced decomposition leads to ring-cyclization, that chain, but only that chain, is stopped; for g = -1, however, the same circumstance leads to interdiction of two chains. As a result, for perester concentrations as high as those employed (i.e., where pairwise destruction of triethyltin radicals is insignificant), % n goes to 100 at zero tin hydride concentration for g = -1, but for g = 0 must stay below about $100[1+\alpha/(1-\beta)]^{-1} = 35$ (compare eqs. 1.9-13 and 1.9-15).

The unsatisfactory fit using g = -1 can not be repaired by choosing a conversion efficiency of less than 100% for evaluation of k_a^{SnH}/k_r; if this were done, the value of k_a^{SnH}/k_r would be smaller and, according to eq. 1.9-14, the values of % n would be found to lie consistently above than those of Calculation 2.

Both treatments assume a constant conversion efficiency for formation of the dihydronaphthalene 10. As such, they fail to account for the drift in the reduced ratios R (calculated from eq. 1.8-5, p. 111) listed in the right-most column of Table 10 and reproduced here as

Table 15. Radical-Induced Decomposition of t-Butyl (γ, γ-Diphenylallyl)peracetate in the Presence of Triethyltin Hydride. Correlation of Percent Normal Decomposition (% n) and Reduced Ratios (R) (From Eq. 1.8-5) Predicted in Various Ways.

Temp. °C	Initial Perester Conc. M	$[Et_3SnH]_o$ M	R	From Ether Yields % n	From Reaction Rates % n	From Mechanistic Treatment % n	R	% n	R
110	0.002	0.010	0.051	25.4 ± 2.4	35.4 ± 7.7	31.3 ± 1.6	0.051	71.1 ± 4.4	0.051
	0.002	0.044	--	--	30.3 ± 3.9	24.4 ± 1.9	--	35.9 ± 4.9	--
	0.002	0.41	--	--	3.6 ± 0.8	7.3 ± 1.2	--	5.7 ± 1.1	--
	0.02	0.67	--	--	3.3 ± 0.6	4.9 ± 0.9	--	3.6 ± 0.7	--
125	0.002	0.010	0.065	32.5 ± 3.2	--	31.6 ± 1.6	0.063	75.8 ± 3.9	0.063
	0.002	0.044	0.059	33.3 ± 7.2	--	25.9 ± 1.8	0.063	41.8 ± 5.2	0.063
	0.002	0.014	0.059	16.6 ± 3.6	--	16.9 ± 2.0	0.063	17.9 ± 3.1	0.063
	0.002	0.39	0.050	5.8 ± 1.9	--	8.8 ± 1.4	0.063	7.2 ± 1.4	0.063
	0.002	0.94	0.043	≤ 3.0	--	4.3 ± 0.8	0.063	3.1 ± 0.6	0.063

Calculation No.	1	2
(k_a^{SnH}/k_r) 110°	6.37	19.60
(k_a^{SnH}/k_r) 125°	5.16	15.87
A(110°)	0.0	∞
B(110°)	0.0	--
γ	0.65	--
δ	--	1.0

Table 15 (Cont.)

	From Mechanistic Treatment							
	% n	R	% n	R	% n	R	% n	R
	30.9 ± 1.2	0.051	30.6 ± 1.2	0.051	33.8 ± 1.4	0.051	34.2 ± 1.4	0.051
	23.3 ± 1.2	--	22.2 ± 1.1	--	26.4 ± 1.5	--	27.3 ± 1.5	--
	5.2 ± 0.5	--	4.1 ± 0.4	--	8.6 ± 1.0	--	9.4 ± 1.0	--
	4.0 ± 0.4	--	3.5 ± 0.4	--	5.2 ± 0.7	--	5.8 ± 0.7	--
	31.3 ± 1.3	0.063	31.1 ± 1.2	0.063	35.0 ± 1.3	0.063	35.3 ± 1.3	0.063
	25.0 ± 1.2	0.061	24.1 ± 1.1	0.060	28.6 ± 1.4	0.067	29.6 ± 1.4	0.063
	15.1 ± 1.0	0.057	13.7 ± 0.9	0.053	18.9 ± 1.4	0.075	20.3 ± 1.4	0.063
	6.8 ± 0.6	0.049	5.6 ± 0.5	0.041	10.5 ± 1.1	0.089	11.6 ± 1.2	0.063
	2.6 ± 0.3	0.038	1.9 ± 0.2	0.028	5.6 ± 0.7	0.106	6.3 ± 0.8	0.063
Calculation No.	3		4		5		6	
$(k_a^{SnH}/k_r$ {110°	6.32		6.27		7.21		6.37	
125°	5.13		5.10		6.02		5.16	
A(110°)	0.0		0.0		0.01		0.01	
B(110°)	0.05		0.10		0.0		0.0	
γ	0.65		0.65		0.65		0.65	
δ	--		--		1.0		0.325	

Table 15 (Cont.)

From Mechanistic Treatment							
% n	R	% n	R	% n	R	% n	R
34.2 ± 1.4	0.051	31.6 ± 1.2	0.051	32.7 ± 1.2	0.051	37.8 ± 1.2	0.051
27.4 ± 1.5	--	23.0 ± 1.2	--	23.1 ± 1.2	--	26.1 ± 1.5	--
9.5 ± 1.0	--	4.6 ± 0.5	--	4.2 ± 0.5	--	4.2 ± 0.5	--
5.8 ± 0.7	--	3.6 ± 0.4	--	3.4 ± 0.4	--	3.4 ± 0.5	--
35.3 ± 1.3	0.063	32.5 ± 1.2	0.063	34.1 ± 1.2	0.063	40.2 ± 1.2	0.063
29.7 ± 1.4	0.063	25.3 ± 1.2	0.062	25.8 ± 1.2	0.062	30.2 ± 1.6	0.068
20.5 ± 1.4	0.062	14.6 ± 1.1	0.059	14.4 ± 1.1	0.060	16.0 ± 1.5	0.068
11.8 ± 1.2	0.060	6.2 ± 0.6	0.052	5.9 ± 0.6	0.053	6.0 ± 0.7	0.057
6.4 ± 0.8	0.058	2.3 ± 0.3	0.042	2.1 ± 0.3	0.041	2.0 ± 0.3	0.042

Calculation No.	7	8	9	10
$(k_a^{SnH}/k_r$ 110°	6.28	6.60	7.05	8.98
$(k_a^{SnH}/k_r$ 125°	5.06	5.46	5.92	7.63
A(110°)	0.01	0.003	0.01	0.01
B(110°)	0.0	0.10	0.15	0.23
γ	0.65	0.65	0.65	0.65
δ	0.25	1.0	1.0	1.0

column 4 of Table 15. Thus, we need to employ the full mechanistic treatment to handle situations close to g = 0, but with some role played by the k_4 and k_5 reactions shown in Chart 5. The definition of g developed in Appendix A is

$$g = \frac{X + B(Et_3SnH)\sqrt{X/(\underset{\frown}{1})} - \underset{\frown}{1}}{X + B(Et_3SnH)\sqrt{X/(\underset{\frown}{1})} + \underset{\frown}{1}} \quad , \qquad (1.9\text{-}16)$$

where $A = (k_4/k_1)(\alpha k_o/k_3)^{\frac{1}{2}}$, $B = k_5/(\alpha k_o k_3)^{\frac{1}{2}}$, and X is a (positive, real) root* of the nonlinear equation

$$X\left[1 + \frac{1.07(k_a^{SnH}/k_r)(Et_3SnH)}{(1-\beta)}\, A\sqrt{X/(\underset{\frown}{1})}\left\{1 + \frac{B(Et_3SnH)}{\sqrt{X(\underset{\frown}{1})}}\right\}\right] + \frac{1.07(k_a^{SnH}/k_r)(Et_3SnH)}{(1-\beta)}\, A\sqrt{X/(\underset{\frown}{1})} = 1 \qquad (1.9\text{-}17)$$

The limiting cases discussed above can be seen rather easily. The case of g = 0 implies small k_4 and/or large k_1 (i.e., A = 0) and small k_5 (i.e., B = 0); with these choices, eq. 1.9-17 gives X = 1, whence eq. 1.9-16 gives g = 0, as expected. The case g = -1 requires large k_4 (i.e., A very large);** that choice forces X to approach 0, and eq. 1.9-16 gives g = -1.

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*When cleared of radicals, eq. 1.9-17 is found to be cubic in X, and thus has three roots. While I have been unable to show that only one of the roots will be real and positive, for all cases investigated that has been the case. Since eq. 1.9-17 is physically motivated, there should be no more ambiguity as to which root is to be taken than occurs for situations in which quadratic equations are involved.

**In practice, this works out to $A \geq 1$.

It is convenient to substitute the general expression for g into eq. 1.9-17 rather than first to explicitly work out numerical values for g for each situation of interest. The resulting expression (which is derived by conventional means in the Appendix, thus confirming the correctness of the treatment given here) is

$$\% \, n = 100 \left[1 + \frac{\alpha}{1-\beta} \left\{ 1.07 (k_a^{SnH}/k_r)(Et_3SnH) \times \left[1 + X + B(Et_3SnH)\sqrt{X/(\underset{\sim}{1})} \right] + X + B(Et_3SnH)\sqrt{X/(\underset{\sim}{1})} \right\} \right]^{-1} . \tag{1.9-18}$$

Finally, the equation for the reduced ratio R is found to be

$$R \equiv \frac{(\text{Yield of } \underset{\sim\sim}{10})\,(Et_3SnH)_{av}}{(\text{Yield of } \underset{\sim}{5})} = \left(\frac{k_r}{k_a^{SnH}} \right) \left[\frac{\gamma X + \delta(1-X)}{1 + X + B(Et_3SnH)\sqrt{X/(\underset{\sim}{1})}} \right] . \tag{1.9-19}$$

where the term in square brackets expresses the efficiency of the conversion of ring-cyclized radicals to dihydronaphthalene. For the two cases g = 0 and g = -1, the conversion efficiencies are simply $\gamma/2$ and δ, respectively.

Because the concentration of ring-opened perester $\underset{\sim}{1}$ appears in eqs. 1.9-16–1.9-19, it is clear that the previous claim--that the induced decomposition is first-order in the perester concentration--is not strictly correct. However, the perester concentration comes in only implicitly; not at all for the combinations A = 0, B = 0, and A large,

B = 0; and only weakly for many intermediate cases.*

The fact that the perester concentration can have some effect, however, will enable us to repair the greatest single discrepancy between the g = 0 predictions and those from ether yields or reaction rates--the high calculated value of % n for the 110° run at 0.4 M tin hydride and 0.002 M perester. If A equals zero, then X simply is unity, and the effect of finite B can clearly be seen from eq. 1.9-18: % n will decrease more rapidly with increasing tin hydride concentration than is the case for g = 0. Thus, agreement for the 0.4 M run can be improved. Note, however, that g = 0 gives a % n at 0.67 M hydride and 0.02 M perester only slightly greater than that deduced from the reaction rate. If, then, a particular value of B were to decrease the predicted % n to the same degree for both the higher hydride concentration runs at 110°, we would have accomplished little more than a sharing of the blame. However, eq. 1.9-18 shows that the new effect is less pronounced at higher perester concentrations, and the already acceptable agreement for the run at 0.02 M initial perester concentration might not be sacrificed.

Calculations 3 and 4 were carried out for values of B (at 110°)** of 0.05 and 0.10, respectively. The drift in the values of R is in the

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*In these calculations, eq. 1.9-18 has been numerically integrated over the course of the reaction using the three point Gaussian quadrature formula (94). The only moderate variation of the three instantaneous % n values for all calculations carried out confirms the adequacy of the three point integration formula.

**The value of B at 125° has been taken in all calculations to be that employed at 110° divided by a factor of 1.3. Justification of this procedure will be given shortly.

proper direction, though of too large a magnitude for the larger value of B. At the same time, the agreement of calculated and "observed" values of % n is distinctly improved for the two highest tin hydride concentrations at 110° and also for the 0.94 M tin hydride run at 125°.

Calculations 5, 6, and 7 explore the consequences of allowing A to be slightly greater than zero.* This corresponds to allowing some ring-cyclized radicals to react with triethyltin radicals. The effect on the conversion efficiency, and thus on the calculated values of the reduced ratio R, depends on whether δ is taken to be greater than, equal to, or less than $\frac{1}{2}\gamma$ (γ = 0.65 in all calculations). In Calculation 5 we have assumed that all reactions of ring-cyclized radicals with tin radicals give rise to the disproportionation products, the dihydronaphthalene 10 and triethyltin hydride (i.e., δ = 1). All predicted % n values are found to be larger than the g = 0 values, with by far the greatest proportionate rise at the higher triethyltin hydride concentrations.**

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*The value of A (110°) employed here is 0.01. In these and other calculations, the value of A employed at 125° has been taken to be 1.5 times the value given in Table 15 for 110°. The justification for this procedure will be given shortly.

**Calculations 5–7 for small A may at first glance seem inconsistent with results for large A (g = -1) obtained in Calculation 2. The connection between Calculations 2 and 5 comes about as follows. As A is increased, g moves from zero toward -1. However, the progression is not uniform, but rather is substantially more advanced at high tin hydride concentration. For example, for 0.94 M tin hydride at 125°, g = -0.5 in Calculation 5, but is scarcely different from zero for the 0.01 M runs. The result is that the values of k_a^{SnH}/k_r which give the desired values of R for the 0.01 M tin hydride runs are substantially the same as those calculated for g = 0. As A continues to be increased, eventually all values of g become substantially negative, and k_a^{SnH}/k_r rises abruptly. The result is to bring together again the values of R at high and low triethyltin hydride concentration and to greatly reduce the calculated values of % n at high tin hydride concentration.

Moreover, the predicted dependence of R on tin hydride concentration is opposite to that observed experimentally. For $\delta = \frac{1}{2}\gamma$ (Calculation 6), the values of R are independent of the tin hydride concentration, but the rise compared to g = 0 in the calculated values of % n is stronger than for $\delta = 1.0$. The trend continues; for $\delta = 0.25$ (Calculation 7), the quantities R show qualitatively the correct behavior, but the agreement between the calculated and "observed" % n values has further decayed. Clearly, there is no future, in seeking a good fit to the data, in continuing this particular line of exploration.

Comparison of Calculations 4 and 5 with Calculation 1 shows that the effects of increasing A and of increasing B on %n and on R are of opposing natures for $\delta > \frac{1}{2}\gamma$. This suggests that it may be possible to increase both A and B concurrently to a far greater extent than is possible singly. Calculations 8, 9, and 10 explore the consequences of this line of reasoning. For B = 0.10, A need only be increased to 0.003 to repair the excessive drift in R with triethyltin hydride concentration reported in Calculation 4. Calculation 9 extends this matching of opposite tendencies to B = 0.15, A = 0.01. The results are gratifying: the drift in R is just right, the % n values for the two higher tin hydride concentration runs at 110° have been moved together as observed experimentally, and the calculated % n for the 0.94 M tin hydride run at 125° remains under the limit set by the yield of the ether 12. However, the vein is soon exhausted; for A = 0.10, and B = 0.23, the overall drift in R is satisfactory, but the values are now incorrectly predicted to increase with increasing tin hydride concentration before finally turning strongly downward.

On balance, Calculation 9 yields the best agreement between calculated and "observed" values of % n. Certain features--the abrupt drop in the yields of the ether 12 with increasing tin hydride concentration and the similar rate constants obtained in the runs featured in Figs. 17 and 18--are well explained. The improvement over the limiting results for g = 0 is substantial. However, it is doubtful that we can take the values of A and B employed in this calculation to have been reliably established. In point of fact, the pairings of initial perester and initial tin hydride which happened to be chanced upon in this work exert insufficient leverage to permit reliable extraction of values for these parameters.

We can, however, tentatively assume that the values of A and B employed in Calculation 9 are reasonable ones and proceed to explore the consequences of this assumption. For each of these two parameters, estimates for all but one of the constituent rate constants can be made with some degree of confidence. This allows approximate values to be derived for the single rate constant in each (k_1 for A and k_5 for B) which is least subject to prediction. Still, it is possible to make a judgement on whether the derived values of k_1 and k_5 are physically realistic. If either is judged to be unrealistic, we would conclude that use has been made of a certain flexibility in our equations, but that no underlying mechanistic significance is to be inferred. On the other hand, an additional measure of confidence in the correctness of the mechanistic treatment would be in order should those estimates prove to be reasonable ones.

In the definition $B = k_5/(\alpha k_o k_3)^{\frac{1}{2}}$, the value of k_o has been found by Howden (21) to be 7.7×10^{-5} M^{-1} sec^{-1} at 110°. The value of the parameter α is about 0.87. The value of the rate constant k_3 for pairwise reaction of ring-cyclized radicals is unknown, but a guess can be formulated from radical-radical termination rate constants reported in the literature. Rate constants quoted by Walling (79) for chain termination in free-radical polymerizations are generally on the order of 10^7 M^{-1} sec^{-1}, although the value listed for vinyl chloride polymerization is 10^{10} M^{-1} sec^{-1}. For small molecule terminations, however, Walling has inferred a value of $\sim 10^9$ for coupling of t-butoxy radicals (82), and preliminary determinations by Weiner (83) for bimolecular reaction of t-butoxy radicals, of α-cyanoisopropyl radicals, and of α-cyanocyclohexyl radicals are all $\sim 3 \times 10^9$ M^{-1} sec^{-1}. We shall adopt a value of 10^8 M^{-1} sec^{-1} for k_3. We therefore find for $B = 0.15$ that $k_5 = 13$ M^{-1} sec^{-1} at 110°. Eq. 1.8-12 shows that preexponential factors for hydrogen abstraction by ring-opened radical $\underset{\sim}{3}$ from 1,4-cyclohexadiene and from triethyltin hydride are nearly the same. This justifies taking the preexponential factor in k_5 to be 10^8, which value is typical for hydrogen abstraction from hydrocarbons. Then the derived value of k_5 at 110° implies an activation energy of approximately 12 kcal/mole.

The question now becomes: is this a reasonable value for the activation energy? Although little is known about activation energies for hydrogen abstraction from organotin hydrides, the following argument can be offered. When all is said and done, our estimate for the activation energy for hydrogen abstraction by the ring-closed radical $\underset{\sim}{4}$

from triethyltin hydride will be approximately 8 kcal/mole (p. 349). By analogy with reported C–H bond dissociation energies of 72 kcal/mole for diphenylmethane and 75 kcal/mole and triphenylmethane (51), the bond dissociation energy for the dibenzylic C–H bond in the ring-closed hydrocarbon 6 can be estimated to lie in the lower or middle seventies. The Sn–H bond dissociation energy in trialkyltin hydrides is not known, but chemical experience is capable of yielding some information. In his 1963 review article, Kuivila suggests a value of approximately 70 kcal/mole for organotin hydrides (41). The C–H bond dissociation energy of the methylene hydrogens in 1,4-cyclohexadiene is reported to be 70 kcal/mole (52). That for the bond formed on converting the ring-cyclized radical 9 to the dihydronaphthalene 10 is expected to be a few kcal/mole less than this value by virtue of the more extensive delocalization in 9 as compared to the cyclohexadienyl radical; perhaps 67 kcal/mole is a reasonable estimate.

Thus we see that abstraction of hydrogen from a given donor by 9 is expected to be less exothermic by approximately 5–10 kcal/mole than is hydrogen abstraction by 4. For hydrocarbon donors, a good correlation exists between the activation energy and the heat of reaction for hydrogen abstraction by alkyl free radicals. For the degenerate (and thus thermoneutral) exchange reaction

$$CH_3\cdot + CH_4 \longrightarrow CH_4 + CH_3\cdot$$

the activation energy is 14 kcal/mole (95), but drops to 9 kcal/mole for abstraction of the tertiary hydrogen of isobutane by methyl radical; the latter reaction is exothermic by approximately 12 kcal/mole (34).

Similar relationships hold for a wide variety of radical-abstraction reactions (53), and such a relationship likely holds for hydrogen abstraction from triethyltin hydride as well. If so, the increased exothermicity for hydrogen abstraction by $\underset{\frown}{4}$ over that for $\underset{\frown}{9}$ is expected to confer on the former process a lower activation energy for hydrogen abstraction from the tin hydride; precisely this behavior is reflected in the independently obtained estimates of 8 and 12 kcal/mole, respectively. Not only is the order of the activation energy estimates correct, but the magnitude of their difference is also reasonable. Finally, the difference of about 5 kcal/mole in the activation energies for hydrogen abstraction by $\underset{\frown}{4}$ from 1,4-cyclohexadiene and from triethyltin hydride (see Fig. 13) is consistent with a Sn–H bond dissociation energy smaller than the 70 kcal/mole C–H bond dissociation energy of 1,4-cyclohexadiene, perhaps on the order of 65 kcal/mole. Thus, hydrogen abstraction by $\underset{\frown}{9}$ is expected to be very nearly thermoneutral, and in this light even the absolute value of 12 kcal/mole estimated for the activation energy of that reaction seems reasonable.

Of the points argued above, the suggested Sn–H bond dissociation energy of 65 kcal/mole rests on the weakest ground, for the tacit assumption that a tin hydride will behave in hydrogen donation like a hydrocarbon donor of equivalent C–H bond dissociation energy is unproven. In many other respects, tin and carbon differ greatly. Specifically, the greater polarizability of the large tin atom may reduce the activation energy characteristic of a thermoneutral abstraction reaction. If this is the case, the activation-energy relationships considered above could be rationalized on the basis of an Sn–H bond

dissociation energy of 70 or even 75 kcal/mole. Conversely, if that quantity were found to be approximately 65 kcal/mole, the assumption of the similarity of carbon and tin in hydrogen abstraction would be supported.

The temperature dependence of B employed in the calculations was derived as follows. The activation energy for B is simply the activation energy of k_5 less one-half the sum of the activation energies of k_o and k_3. By analogy with activation parameters for perester decomposition given in Table 13, that for the normal decomposition of the ring-opened perester is expected to be about 34 kcal/mole. Activation energies for rapid radical-radical reactions tend to run about 2 kcal/mole (96). The origin of this token value is presumably the more rapid diffusion of particles at the lower solution viscosities which are associated with higher reaction temperatures. Thus, the predicted composite activation energy for B is -6 kcal/mole, and the value of B at 125° is that at 110° divided by 1.3.

The rate constants k_o and k_3 also appear in $A = (k_4/k_1)(\alpha k_o/k_3)^{\frac{1}{2}}$, where the rate constant for bimolecular reaction (disproportionation or coupling) of $\underset{\sim}{9}$ with a triethyltin radical is denoted by k_4, and that for attack of tin radical on the perester is denoted by k_1. If we take k_o and k_3 as before and arbitrarily set $k_4 = k_3$, we find that $A = 0.010$ implies $k_1 = 10^4\ M^{-1}\ sec^{-1}$ at 110°. As k_1 is an abstraction reaction, we will perhaps not be too seriously in error if we assign as its pre-exponential factor a value of 10^8 motivated by experience with hydrogen atom abstraction reactions. The associated activation energy is

easily found to be 7 kcal/mole.* This already is an encouraging result: if the value found for A were of no mechanistic significance, a physically impossible estimate of the activation energy for k_1, such as a negative value, might have resulted. The activation energy of 7 kcal/mole and the rather large value estimated for k_1 seem respectable, however, when we recall that triethyltin radicals are in fact diverted to attack on perester, whereas hydrocarbon radicals (such as cyclohexadienyl radical) enjoy the more leisurely hunting up of a second free radical for the purpose of mutual annihilation.

The explanation for the divergent behavior of tin and hydrocarbon radicals is apparently to be found in a consideration of bond dissociation energies. If we consider that the choice faced by either type of radical is between formation of a bond to hydrogen (disproportionation with 9) or a bond to oxygen, the following comparison is relevant. The C–H bond dissociation energy in methane is 102 kcal/mole, whereas the C–O bond dissociation energy in methanol is given by Cottrell as approximately 90 kcal/mole (97). Thus, for alkyl radicals formation of a C–O bond is less exothermic than formation of a C–H bond by about 12 kcal/mole. This order is reversed for tin radicals; the dissociation energy of the Sn–O bond of trimethyltin

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*This value leads to a composite activation energy of 9 kcal/mole for A. In Calculations 5–10 of Table 15 the value of A at 125° has been taken to be that at 110° times 1.6, where the factor of 1.6 arises from the 9 kcal/mole composite activation energy.

benzoate is roughly 115–120 kcal/mole,* whereas the Sn–H bond dissociation energy, according to our previous discussion, is only about 65 kcal/mole. Thus we see that formation of a Sn–O bond is approximately 50 kcal/mole more exothermic than formation of a Sn–H bond, and the difference between tin and carbon in this respect is fully 60 kcal/mole.

Although induced decomposition is exothermic both for carbon and for tin radical, this large thermochemical difference surely provides a driving force for making induced decomposition decidedly more attractive in the case of the latter.

The following experimental observations are of interest in regard to the effect of temperature on the relative facility of formation of tin ester and tin ether upon attack of triethyltin radicals on the ring-opened perester 1. Experiments thus far reported apply to degassed reaction mixtures heated to 110–125°. However, in the presence of air, decomposition of 1 in solutions containing triethyltin hydride proceeds at measurable rates even at room temperature. For example, the half-life of perester at room temperature (about 23°) of a solution 0.72 M in triethyltin hydride and 0.02 M in 1 was found to be roughly 3 hours. Solutions 0.002 M in 1 and 0.4 M or 0.048 M in tin hydride

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*The experimental observation is that the thermochemical Sn–O bond energy, as obtained from heats of formation and of atomization, is 95 kcal/mole (98). However, Yergey and Lampe have recently shown that the actual bond dissociation energies for Sn–X bonds (X = Br, I, alkyl, aryl) are 20–21 kcal/mole higher than the thermochemical bond energies (99). They attribute the difference to a reorganization energy for the tin radical. I have added this correction to the thermochemical Sn–O bond energy to obtain the bond dissociation energy quoted.

displayed half-lives of about 6 and 50 hours, respectively. Presumably the agent initiating the induced decomposition is oxygen from the air (which is known to readily attack organotin hydrides): a sample of the run 0.72 M in triethyltin hydride maintained for 3 hours at about 10^{-4} mm showed negligible or nonexistent buildup of tin ester.

Interestingly, the yields of tin ester in these air-induced decompositions were on the order of 90%. This figure is to be compared to yields of 55% (i.e., $\beta = 0.55$) at 110 to 125°. Thus, the partitioning between radical attack leading to formation of tin ester and that leading to formation of tin ether must be appreciably temperature dependent, with the latter process having the higher activation energy.

Unfortunately, several factors conspired to make impossible the precise determination of the yield tin ester in the air-induced experiments. It turns out that the tin hydride has sufficient absorbance at 1651 cm^{-1} (the carbonyl maximum for the tin ester) to require that corrections be made to absorbances measured there. The application of these corrections is complicated by the fact that the concentration of tin hydride can easily be diminished (through air oxidation) by a factor of two or more before sufficient time has elapsed to permit taking the yield of ester to represent the limiting yield. In addition, tin hydrides do add to olefins (such as the tin ester 14). Thus, the yield of tin ester may well pass through a maximum which lies below the true limiting yield of tin ester as controlled by relative amounts of the two kinds of attack on perester. Indeed, the true limiting yield may easily be as low as 85% or as high as 95%. In assessing the difference in activation energies for the two modes of radical attack, an

uncertainty of this magnitude is quite significant. The estimate of 90% implies that the activation energy for attack on perester to give tin ether is 4.7 kcal/mole greater than that for attack to give tin esther. A limiting yield of 95% at room temperature would imply an activation energy difference of 6.3 kcal/mole.

APPENDIX A. Kinetic Treatment of Induced Decomposition in the Presence of Triethyltin Hydride

The purpose of this appendix is to derive eqs. 1.9-16--1.9-19 via conventional steady-state kinetics. All rate processes considered here are depicted in Chart 5, p. 161. We begin by writing down the rate law expressions for the steady-state free-radical intermediates Sn·, R·, and R'·. The latter symbol denotes the ring-cyclized radical $\underset{\sim}{9}$, and, as in the earlier treatment, P stands for the ring-opened perester $\underset{\sim}{1}$.

$$d(Sn\cdot)/dt = \alpha k_o(P) - (1-\beta)k_1(Sn\cdot)(P) + k_{ab}(R\cdot)(Et_3SnH) + k_5(R'\cdot)(Et_3SnH) - k_4(Sn\cdot)(R'\cdot) = 0 \quad (A1)$$

$$d(R\cdot)/dt = \alpha k_o(P) + (1-\beta)k_1(Sn\cdot)(P) - k_{ab}(R\cdot)(Et_3SnH) - k_r(R\cdot) = 0 \quad (A2)$$

$$d(R'\cdot)/dt = k_r(R\cdot) - k_5(Et_3SnH)(R'\cdot) - 2k_3(R'\cdot)^2 - k_4(Sn\cdot)(R'\cdot) = 0 \quad (A3)$$

The term $k_2(Sn\cdot)^2$ has been omitted in eq. 1 for reasons discussed in subsection 9.

We now add together eqs. 1, 2, and 3, and solve for (Sn·):

$$(Sn\cdot) = \frac{\alpha k_o(P) - k_3(R'\cdot)^2}{k_4(R'\cdot)} \quad (A4)$$

Note that eq. 4 involves Sn· and R'· , but not R· . We can obtain a second equation in Sn· and R'· by solving each of eqs. 2 and 3 for (R·) and equating the resulting expressions:

$$\alpha k_o(P) + (1-\beta)k_1(Sn\cdot)(P) = \left(1 + E(Et_3SnH)\right)\left\{k_5(Et_3SnH)(R'\cdot) + 2k_3(R'\cdot)^2 + k_4(Sn\cdot)(R'\cdot)\right\} \tag{A5}$$

where $E = k_{ab}/k_r$ (k_{ab} is defined in eq. 1.9-10).

Eq. 4 is now substituted into eq. 5 to eliminate (Sn·). Rearrangement of the resulting equation leads to:

$$\frac{k_3(R'\cdot)^2}{\alpha k_o(P)}\left[1 + \frac{(1+E(Et_3SnH))}{(1-\beta)k_1(P)}k_4(R'\cdot)\left\{1 + \frac{k_5(Et_3SnH)}{k_3(R'\cdot)}\right\}\right] + \frac{E(Et_3SnH)k_4(R'\cdot)}{(1-\beta)k_1(P)} = 1 \tag{A6}$$

We now make the following definitions:

$$X = \frac{k_3(R'\cdot)^2}{\alpha k_o(P)}\ ; \qquad A = \frac{k_4}{k_1}\left(\frac{\alpha k_o}{k_3}\right)^{\frac{1}{2}}\ ; \qquad B = \frac{k_5}{(\alpha k_o k_3)^{\frac{1}{2}}}\ .$$

Substitution of these quantities in eq. 6 is readily seen to give eq. 1.9-17 (p. 175).

The probability function g introduced in subsection 9 is defined to be the probability that conversion of ring-cyclized radical $\underset{\sim}{9}$ to product occurs with the generation of a triethyltin radical. As noted previously, the term probability is not completely accurate, for we

mean to account as well for the possibility that conversion of $\underset{\sim}{9}$ to product consumes a triethyltin radical. That is, $-1 \leq g \leq 1$. In terms of rate constants defined in Chart 1, we must have

$$g = \frac{k_5(Et_3SnH)(R'\cdot) - k_4(Sn\cdot)(R'\cdot)}{2k_3(R'\cdot)^2 + k_5(Et_3SnH)(R'\cdot) + k_4(Sn\cdot)(R'\cdot)} \qquad (A7)$$

inasmuch as the k_3, k_4, and k_5 processes are assumed to be the only reaction steps open to ring-cyclized radicals. Substituting for $(Sn\cdot)$ from eq. 4 and rearranging gives

$$g = 1 - 2\left[1 + \frac{k_3(R'\cdot)^2}{\alpha k_o(P)} + \frac{k_3(Et_3SnH)(R'\cdot)}{\alpha k_o(P)}\right]^{-1} . \qquad (A8)$$

At first glance eq. 8 does not seem to be much of an improvement on eq. 7, but it indeed turns out that application of the definitions of X, A, and B reduces eq. 8 to a relatively simple form:

$$g = \frac{X + B(Et_3SnH)\sqrt{X/(P)} - \underset{\sim}{1}}{X + B(Et_3SnH)\sqrt{X/(P)} + \underset{\sim}{1}} \qquad (A9)$$

Eq. 9 is identical to eq. 1.9-16.

As noted in subsection 9, eq. 1.9-18 (which relates % n directly to quantities developed in this Appendix) can be obtained by substituting 9 into an expression previously derived by a rather unconventional treatment which was drawn in terms of the probabilities that the reaction takes certain paths leading from two key branch points. We wish to show here that the treatment given previously was indeed a

valid one. This will be done by deriving eq. 1.9-18 directly, According to eq. 1.9-2, the percent normal decomposition is given by

$$\% \, n = 100 \left[1 + k_1 (Sn\cdot) / k_o \right]^{-1} \quad , \tag{A10}$$

where this expression is to be averaged over the course of the reaction if (Sn·) is not independent of (P). Eq. 4 can be rewritten in terms on the quantities A and X in the form

$$(Sn\cdot) = \frac{\alpha k_o (P)}{k_1} \left[\frac{1 - X}{A\sqrt{X/(P)}} \right] \quad . \tag{A11}$$

Eq. 11 is of limited usefulness, however, because we are interested in situations in which A is equal, or nearly equal, to zero, and both the numerator and the denominator of the term in square brackets vanish at A = 0. However, eq. 1.9-17 (or eq. 6) can be rearranged to the form

$$\frac{(1 - X)}{A\sqrt{X/(P)}} = \frac{1}{(1-\beta)} \left\{ E(Et_3SnH) \left[1 + X + B(Et_3SnH) \sqrt{X/(P)} \right] + X + B(Et_3SnH)\sqrt{X/(P)} \right\} . \tag{A12}$$

in which the right-hand side is well behaved. Thus, we can substitute from eq. 12 for the term in square brackets in eq. 11 and put the resulting expression into eq. 10. The equation thereby obtained is identical with eq. 1.9-18:

$$\% \, n = 100\left[1 + \frac{\alpha}{(1-\beta)}\left\{E(Et_3SnH)\left[1 + X + B(Et_3SnH)\sqrt{X/(P)}\right] + X + B)Et_3SnH)\sqrt{X/(P)}\right\}\right]^{-1} \tag{A13}$$

Next, the reduced ratio R is given by

$$R = \frac{(\text{Yield of } \underset{\sim}{10})(Et_3SnH)_{av}}{(\text{Yield of } \underset{\sim}{5})} = \left(\frac{k_r}{k_a^{SnH}}\right)\left[\frac{\gamma k_3(R'\cdot)^2 + \delta k_4(Sn\cdot)(R'\cdot)}{2k_3(R'\cdot)^2 + k_5(Et_3SnH)(R'\cdot) + k_4(Sn\cdot)(R'\cdot)}\right] \tag{A14}$$

As with eq. 7, the original equation for the probability function g, the denominator of the term in square brackets expresses the totality of the reactions open to ring-cyclized radicals under our mechanistic assumptions, and the numerator is comprised of those reactions which lead to the desired result, in this case conversion of ring-cyclized $\underset{\sim}{9}$ to the dihydronaphthalene $\underset{\sim}{10}$. Therefore, the term in square brackets represents the efficiency of conversion of $\underset{\sim}{9}$ to $\underset{\sim}{10}$. Introduction of the quantities A, B, and X puts eq. 14 into the form*

$$R = \left(\frac{k_r}{k_a^{SnH}}\right)\left[\frac{\gamma X + \delta(1-X)}{1 + X + B(Et_3SnH)\sqrt{X/(P)}}\right] \quad . \tag{A15}$$

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*Conceptually, the approach taken here is incorrect. We really ought to have developed expressions for the yields of $\underset{\sim}{5}$ and of $\underset{\sim}{10}$, integrated these expressions numerically, and then taken the ratio of the resulting numbers as in eq. 1.8-5; this is the approach taken in Section Two. However, as the quantity R does not vary greatly with perester concentration, the error in the treatment employed here is negligible.

Finally, we shall show that decyclization of ring-cyclized radical $\underset{\sim}{9}$ to ring-opened radical $\underset{\sim}{3}$ (rate constant k_{-r}) is mechanistically unimportant under the present conditions. Inclusion of this step would modify eqs. 2 and 3 by addition of the term $k_{-r}(R'\cdot)$ to the former and subtraction of the same term from the latter, so that eq. 4, the sum of eqs. 1, 2, and 3, would be unchanged. Eqs. 5 and 6 would differ, but the resulting equation for the variable X (eq. 1.9-17) would be unchanged if we make the definition

$$B \equiv \frac{k_5}{(\alpha k_o k_3)^{\frac{1}{2}}} + \frac{E}{1 + E(Et_3SnH)}\left(\frac{k_{-r}}{k_3^{\frac{1}{2}}}\right)\left(\frac{1}{\alpha k_o}\right)^{\frac{1}{2}} .$$

As eq. 6 was used directly in obtaining eq. 13, this definition of B is also appropriate for calculation of % n values.

The new term on the right-hand side is evaluated as follows. For satisfactory calculations in Table 15, $k_a^{SnH}/k_r \cong E$ is about 7 liters/mole. The factor of $k_{-r}/k_3^{\frac{1}{2}}$ arises in the mechanistic treatment of Section Two, where an upper limit of 5×10^{-5} (liter-sec/mole)$^{-\frac{1}{2}}$ at 100° is inferred (heading Q, p. 287). The analogous value at 110° is 10^{-4} according to the assumed composite activation energy of 18 kcal/mole quoted there. The value of k_o at 110° is 7.7×10^{-5} sec^{-1} (21). Thus, we find with $\alpha \cong 0.9$ that the new term has a value of ≤ 0.08 for zero triethyltin hydride concentration. As the discussion under heading Q indicates that $k_{-r}/k_3^{\frac{1}{2}}$ and $k_o^{\frac{1}{2}}$ must have almost identical activation energies, this value is appropriate at 125° as well. Although this value is similar to values of B employed in various calculations in Table 15,

this will not of itself much affect the calculations because the calculations are sensitive to values of B in the range employed only for the higher tin hydride concentrations; the important factor is the product $B(Et_3SnH)$. And the value of 0.01 for the new term at 0.94 M tin hydride, the highest hydride concentration employed, is easily neglectable with respect to values of B employed in the calculations.

For the reduced ratio R, one again finds that allowance for the decyclization may be made by redefining the parameter B, but this time we require

$$B(Et_3SnH) \equiv \frac{k_5(Et_3SnH)}{(\alpha k_o k_3)^{\frac{1}{2}}} + \left(\frac{k_{-r}}{k_3^{\frac{1}{2}}}\right)\left(\frac{1}{\alpha k_o}\right)^{\frac{1}{2}} \quad .$$

The value of the second term on the right-hand side is ≤ 0.01 according to estimates quoted above. The results for calculations displayed in Table 15 show that for values of B of about 0.1, the reduced ratios are strongly affected only for the higher tin hydride concentrations, or for values of about 0.1 for the product $B(Et_3SnH)$. Thus, the correction term is insignificant. Even if data considered in Section two permitted the ratio $k_{-r}/k_3^{\frac{1}{2}}$ to be an order of magnitude larger than was found to be the case, however, the revised definition shows that decyclization would not cause the reduced ratios to vary significantly with the hydride concentration, but would instead rather uniformly increase the denominator in eq. 15 and thus simply distort values of k_r/k_a^{SnH} inferred by fitting reduced ratios to eq. 15.

SECTION TWO: NUMERICAL EVALUATION OF THE REACTION MECHANISM

The purpose of this section is to give a quantitative mechanistic description of a complex set of processes which occurs when either of the peresters t-butyl (γ, γ-diphenylallyl)peracetate (1) or t-butyl diphenylcyclopropylperacetate (2) is allowed to decompose thermally in the presence of 1, 4-cyclohexadiene. The relevant experimental observations are listed in Tables 1, 2, 4, 5, and 6. Those observations have been discussed qualitatively in Section One, principally in subsection 8A. The present quantitative description will allow us to firmly establish a number of points which could be postulated, though not proven, on the basis of qualitative reasoning and to suggest the existence of other factors which may be detected only by examining the adequacy of mechanistic expressions derived with and without their inclusion.

We begin by introducing the reaction steps to be considered and presenting appropriate mechanistic expressions in subsection 1. The derivation of the mechanistic expressions is handled in Appendix B. A formalism for fitting expressions of arbitrary form in the sense of least squares is then described in subsection 2 and applied to the case at hand in subsection 3. Finally, results of the mechanistic treatment are presented in subsection 4.

It is to be expected that many readers will be presently unconcerned with the details of the least-squares adjustment. Such readers

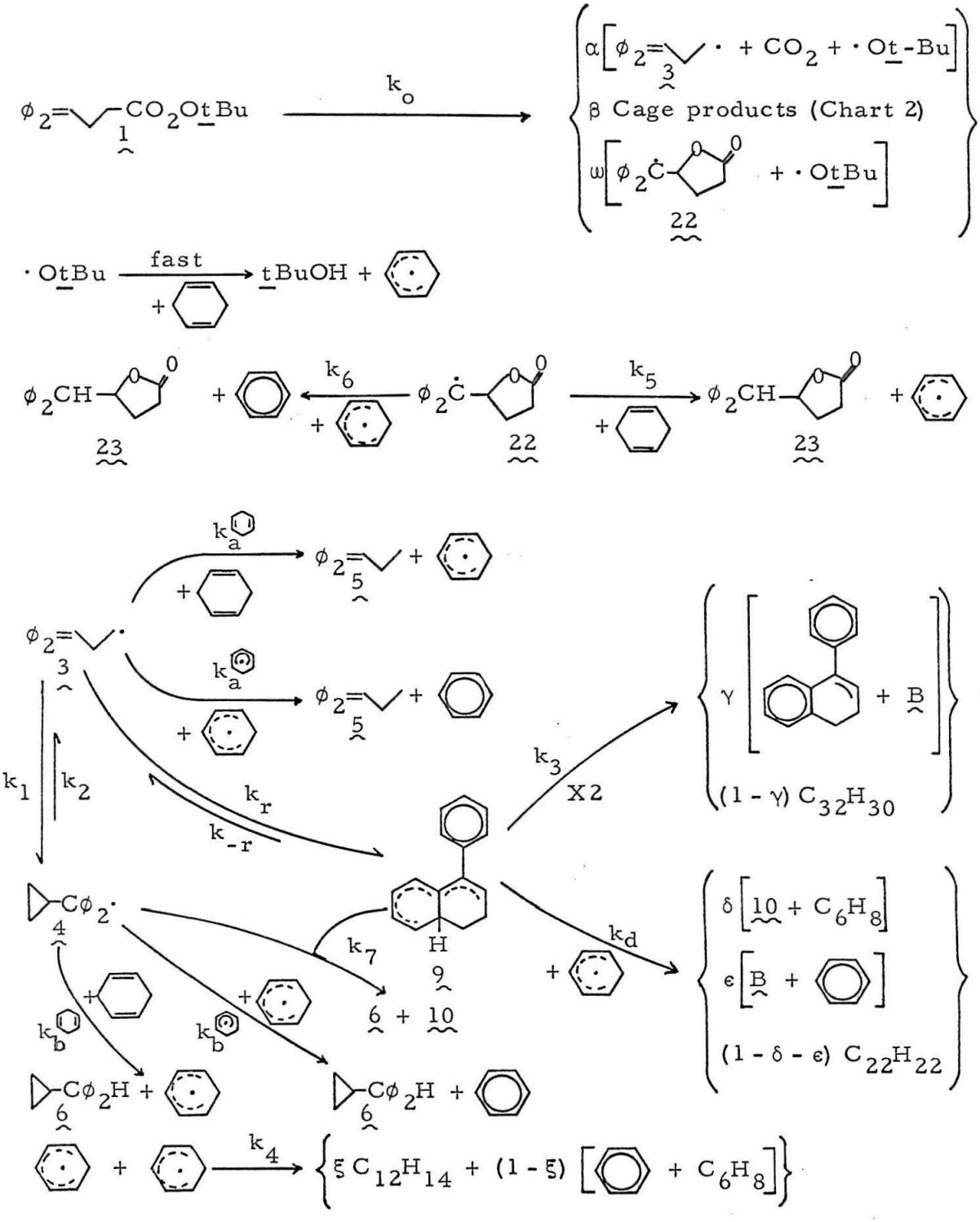
may wish to read subsection 1 and then go directly to the presentation of results in subsection 4. Moreover, a five page summary of the principal conclusions of subsection 4 (pp. 290–295) has been provided. Some may wish to read that summary and refer to the original treatment only for points which seem especially interesting. Subsection 4 itself has been heavily indexed to ensure a sense of direction and to allow readers to pick and choose among areas to be examined.

1. Expressions for Yields and Ratios of Three Key Products

All of the types of reaction steps we shall consider are depicted in Chart 7. That chart assumes that the starting perester is the ring-opened perester 1, but only upper portion would be different for decomposition of the ring-closed perester 2.

Decomposition of the perester is shown at the top of the chart. A certain variable fraction α of such events leads to a kinetically free radical pair composed of ring-opened radical 3 and a t-butoxy radical. Another fraction β represents those events which result in formation of cage-reaction products, in this case the ring-opened ether 12 and the butadiene 13 of Chart 2, p. 58; here we are not interested in the identity of the cage products, but merely seek to take the fact of their formation into account. Lastly, we take molecule-induced decomposition (Section One, subsection 6) to make up a fraction w of the decomposition events, where $\alpha + \beta + \omega = 1$. For decomposition of ring-closed perester 2, we would have $\omega = 0$ and the hydrocarbon radical formed with probability α would be the ring-closed radical 4.

Chart 7. Mechanistic scheme for decomposition of t-butyl (γ, γ-diphenylallyl)peracetate in the presence of 1,4-cyclohexadiene.



As rapid equilibration of 3 and 4 has already been established for decomposition of the peresters in 1,4-cyclohexadiene (see also p. 253), the identity of the first-formed hydrocarbon radical is immaterial.

We dispense with further consideration of the t-butoxy radical by postulating its rapid and certain abstraction of hydrogen from 1,4-cyclohexadiene.*

The nest process shown is conversion of the lactonyl radical 22 to the lactone 23. Two pathways are provided; abstraction of hydrogen from 1,4-cyclohexadiene or from cyclohexadienyl radical.** The reason for postulating a radical-radical reaction here but not for consumption of t-butoxy radical (or methyl radical) is that whereas hydrogen abstraction from cyclohexadiene by the latter is exothermic by more than 30 kcal/mole, the analogous process for the dibenzylic lactonyl radical 22 is expected to be very nearly thermoneutral, and thus will sport a much smaller rate constant. However, the rates of the radical-radical processes are expected to be rather similar. The level of radical concentrations which can be predicted thus allow neglect of the radical-radical process in the case of the t-butoxy radical,

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*Actually, β-scission may also occur--and because of the remarkable augmentation of that process noted in olefinic solvents (42, 43), might be significant. But then the resulting methyl radical would effect the hydrogen abstraction. The assumption is that one cyclohexadienyl radical results for each kinetically free t-butoxy radical produced in the decomposition of the perester, but how this comes about is not of interest.

**This description is only approximate in that lactonyl radicals undoubtedly react with radicals other than cyclohexadienyl. However, cyclohexadienyl radicals are expected to be the most prevalent, and are the logical choice for inclusion in an approximate treatment (which is all that is really needed).

but not in the case of the lactonyl radical. This is a matter of potential importance, since the product ratios of interest (vide infra) depend on the concentration of cyclohexadienyl radicals, which concentration can be augmented or diminished depending on the pathway chosen by the lactonyl radicals.

We now come to a block of interconnecting reactions which are intended to account for formation of three key hydrocarbons: the ring-opened 5; the ring-closed 6; and the ring-cyclized 10. The rate constants k_1 and k_2 relate to the interconversion of the ring-opened and ring-closed radicals 3 and 4. Lengths of the arrows indicate the position of equilibrium which, according to arguments given earlier (p. 138), lies on the ring-closed side (see also heading K, p. 277). Each of the radicals may abstract hydrogen either from 1,4-cyclohexadiene (the k_a ⬡ and k_b ⬡ processes) or from cyclohexadienyl radical (the k_a ⬡ and k_b ⬡ processes). From subsection 8A of Section One we know that 3 employs mainly the first type of process and 4, mainly the second.

We have assumed that ring-opened radical 3 is the species which undergoes ortho-ring cyclization to ring-cyclized 9.

Because interconversion of 3 and 4 is much faster than any other processes of which they partake, our final equations and results will be interpretable in terms of alternative formulations in which a species such as the nonclassical homoallylic radical 7 plays a part. However, we shall assume in the present section that the radicals 3 and 4 play the roles assigned them in Chart 7; other possibilities will be briefly considered in Section Three.

The rate constant for ring-cyclization is denoted by k_r and that for decyclization, by k_{-r}. Again, the lengths of the arrows are suggestive; we have already shown that decyclization is not an important reaction under the present conditions (pp. 114, 115). The reason for its inclusion here is to allow us to determine just how small k_{-r} must be, this by way of fully justifying the omission of decyclization in the mechanistic treatment given earlier of radical-induced decomposition in triethyltin hydride.

Several ways by which ring-cyclized radicals might be converted to non-radical products are included in this mechanistic treatment. Reaction of a pair of ring-cyclized radicals may lead to disproportionation (probability = γ) or to dimerization (probability = $1 - \gamma$). Similarly, reaction of a ring-cyclized radical with a cyclohexadienyl radical (rate constant k_d) may lead to disproportionation or to coupling, but now the disproportionation may occur in two ways, one leading to dihydronaphthalene $\underset{\sim}{10}$ (probability = δ) and the other to one of the tetrahydronaphthalenes $\underset{\sim}{B}$ (see Chart 4, p. 78) (probability = ϵ). The probability of coupling, then, is $1 - \delta - \epsilon$. Finally, disproportionation of $\underset{\sim}{9}$ with the relatively stable ring-closed radical $\underset{\sim}{4}$ (rate constant k_7) has been included by way of accounting for formation of small amounts of $\underset{\sim}{6}$ in indene (Table 7) where solvent-derived radicals can not supply the necessary hydrogen atom and there is a good reason to think that hydrogen abstraction from indene itself would not be effective.

Lastly, the rate constant for pairwise reaction of cyclohexadienyl radicals is denoted by k_4.

The mechanistic scheme makes no provision for the possibility that the coupling products indicated by empirical formulas in Chart 7 might redissociate on the time scale of the perester decompositions. As ring-cyclized radicals and cyclohexadienyl radicals are relatively stable radicals, this assumption requires some justification. Fortunately, observed yields of cyclohexadienyl radical dimer appear to provide the desired justification (see subsection 4, p. 285).

As in the earlier treatment of induced decomposition in the presence of triethyltin hydride, the tough job--the actual algebraic manipulation of equations resulting from the processes of Chart 7--will be handled in an appendix (Appendix B). We will give here only the resulting mechanistic equations. Even these, however, can be pretty awesome.

We will be primarily interested in expressions for the product ratios R1 ≡ % yield $\underset{\sim}{5}$/% yield $\underset{\sim}{10}$ and R2 ≡ % yield $\underset{\sim}{6}$/% yield $\underset{\sim}{5}$. Expressions for the three product yields are given in eqs. 2.1-1, -2, and -3. Each takes the form of an integral over the course of the reaction, the integration variable $z \equiv (P)/(P)_o$ being the ratio of perester concentration part way through the reaction period to the initial concentration.

$$\%\ \text{yield}\ \underset{\sim}{5} = 100\alpha \int_0^1 \left\{ E^*(ZH) + (G/H)^* \left(\frac{\alpha k_o (P)_o z}{2X} \right)^{\frac{1}{2}} \right\} W^* dz \qquad (2.1\text{-}1)$$

$$\%\ \text{yield}\ \underset{\sim}{6} = 100\alpha \int_0^1 \left\{ E^* I^* (ZH) + G \left(\frac{\alpha k_o (P)_o z}{2X} \right)^{\frac{1}{2}} \left[1 + \frac{4C^* W}{S(1+T)} \right] \right\} W^* dz \qquad (2.1\text{-}2)$$

$$\% \text{ yield } \underset{\sim}{10} = 100\alpha \int_0^1 \frac{2}{S(1+T)} \left\{ \delta + \frac{4W^*X^*\gamma}{S(1+T)} + G^*C^*W \sqrt{2\alpha k_o (P)_o z X} \right\} W^* dz \quad (2.1\text{-}3)$$

Aside from the integration variable z, four types of quantities appear in the above equations and in other mechanistic equations recorded below or in Appendix B. As it will be necessary to distinguish between the four classes in the least-squares analysis, we shall give them names.

First we have the adjustable parameters. These are the independent quantities which may be varied to effect the best possible agreement between calculated and observed product ratios. These include the arabic letters A through I and the Greek letters γ and δ. The arabic letters represent combinations of rate constants from Chart 7 which appear together in the mechanistic equations:

$$A = \frac{\omega}{\alpha} \qquad D = \frac{k_{-r}}{k_3^{\frac{1}{2}}} \qquad G = \frac{k_1 k_b^{\textcircled{\scriptsize O}} k_3^{\frac{1}{2}}}{k_2 k_r k_d}$$

$$B = \frac{k_5 k_d}{k_6 k_3^{\frac{1}{2}}} \qquad E = \frac{k_a^{\textcircled{\scriptsize I}}}{k_r} \qquad H = \frac{k_1 k_b^{\textcircled{\scriptsize O}}}{k_2 k_a^{\textcircled{\scriptsize O}}} \qquad (2.1\text{-}4)$$

$$C = \frac{k_7 k_d}{k_b^{\textcircled{\scriptsize O}} k_3} \qquad F = \frac{k_3 k_4}{k_d^{\,2}} \qquad I = \frac{k_1 k_b^{\textcircled{\scriptsize I}}}{k_2 k_2^{\textcircled{\scriptsize I}}}$$

For purposes of orientation, it will be helpful to quickly run through a description of the roles played by the arabic-letter parameters:

A measures the extent of molecule-induced decomposition of perester 1.

B controls the competition between hydrogen abstraction by lactonyl radicals 22 from 1,4-cyclohexadiene and from cyclohexadienyl radical.

C measures the facility of reaction of 4 with 9 with respect to the more important reaction of 4 with cyclohexadienyl radical.

D provides for the possibility of decyclization.

E is the rate-constant ratio which together with the 1,4-cyclohexadiene concentration, controls the partitioning of ring-opened radicals between hydrogen abstraction and ring-cyclization.

F measures the respective tendencies toward self- and cross termination in a system containing ring-cyclized radicals and cyclohexadienyl radicals. It has a statistical value (100) of 0.25.

G is composed of rate constants which determine the rate of formation of ring-closed hydrocarbon 6 from 4 plus cyclohexadienyl radical relative to the rate of formation of 9 via the ortho-ring cyclization process. Thus 6/E is an important determinant of the product ratio R2.

H is the characteristic ratio 6:5 (p. 13) arising via hydrogen abstraction from cyclohexadienyl radicals by 3 and by 4.

I is the analogous quantity for hydrogen abstraction from 1,4-cyclohexadiene.

The observables are those quantities which can be measured or inferred experimentally. Examples are: $(ZH)_o$, the initial concentration of the active hydrogen donor, 1,4-cyclohexadiene; and k_o and $(P)_o$ which denote the rate constant for thermal decomposition of the starting perester and the initial concentration of that perester. Other observables include the reaction temperature (not the 'T' in the above equations) and the experimentally measured values of the ratios R1 and R2 and of the yield of 5.

The third category is comprised of the variables X and W. As with the 'X' of the kinetic treatment of induced decomposition in triethyltin hydride, these arise from the steady-state equations describing the formation and destruction of radical intermediates. Their definitions will be given shortly.

The fourth and last category is made up of the quantities S and T; these are merely shorthand symbols for subexpressions constructed from the first three types of quantities:

$$S \equiv 1 + D*\left(\frac{\alpha k_o(P)}{2X}\right)^{-\frac{1}{2}} + G*C*W(2\alpha k_o(P)*X)^{\frac{1}{2}} \qquad (2.1\text{-}5)$$

$$T \equiv \{1 + 16W*X/S^2\}^{\frac{1}{2}} \qquad (2.1\text{-}6)$$

In Appendix A for induced decomposition in triethyltin hydride, we were able to obtain from the steady-state rate equations an equation involving the concentration of a single one of the several free-radical intermediates. At that point it became convenient to define a dimensionless variable X by grouping certain key rate constants with the concentration of the free radical in question. That gave a nonlinear equation in X, and the desired mechanistic equations were expressed in terms of a particular root of the 'X equation'.

The situation in Appendix B is similar, except that we come down to a system of two simultaneous nonlinear equations in the concentrations of a pair of radical intermediates. Our results are therefore expressed in terms of the dimensionless variables W and X,

$$W \equiv k_r(\hat{3})/\{\alpha k_o(P)\} \tag{2.1-7}$$

$$X \equiv \alpha k_o(P) k_3/\{2k_d{}^2(Z\cdot)^2\} \tag{2.1-8}$$

where $(Z\cdot)$ is the concentration of cyclohexadienyl radicals. The two equations which W and X must simultaneously satisfy are:

$$\frac{1 + \dfrac{2W*D}{S(1+T)}\left(\dfrac{\alpha k_o(P)}{2X}\right)^{-\frac{1}{2}}}{1 + E*(1+I)*(ZH) + G*(1+1/H)*\left(\dfrac{\alpha k_o(P)}{2X}\right)^{\frac{1}{2}} + \dfrac{2G*C*W(2\alpha k_o(P)X)^{\frac{1}{2}}}{S(1+T)}} - W = 0 \tag{2.1-9}$$

$$1 + W*\left\{E*(1+I)(ZH) + G*(1+1/H)*\left(\frac{\alpha k_o(P)}{2X}\right)^{\frac{1}{2}}\right\} + 2A*\left\{\frac{B*(ZH)*\left(\dfrac{\alpha k_o(P)}{2X}\right)^{-\frac{1}{2}}}{1 + B*(ZH)*\left(\dfrac{\alpha k_o(P)}{2X}\right)^{-\frac{1}{2}}}\right\} - \frac{2}{S(1+T)} - F/X = 0 \tag{2.1-10}$$

Values of the variables W and X are extracted using a generalization of the Newton-Raphson method (101) starting from approximate values obtained from empirical relationships.

Finally, because 1, 4-cyclohexadiene is consumed in the reaction, the (ZH) appearing in eqs. 2.1-1— -10 will not be the same as the initial concentrations recorded in the data tables. The procedure employed for making the necessary corrections is explained in Appendix B.

A computer program is rather obviously required to handle eqs. 2.1-1–2.1-10. Several approaches are conceivable. One would be to perform the calculations for several sets of values of the unknown parameters and to examine the results to determine which sets give a good fit to the observed product ratios. This was the general approach taken for induced decomposition in triethyltin hydride. Here, however, such an approach would result in utter confusion because of the large number of parameters involved.

The other extreme would be to include all of the parameters in the least-squares optimization. However, this would be improper because the least-squares criteria concern only the product ratios R1 and R2, whereas some consideration of actual yields must be provided. We shall do this by restricting γ and δ to values which lead to yields of the ring-opened hydrocarbon $\underset{\sim}{5}$ which are of the correct magnitude on the average.* In addition, the parameter A must be chosen to reproduce yields of the lactone $\underset{\sim}{23}$ rather than to best fit the product ratios R1 and R2.

The procedure actually employed is thus a compromise between two extremes. The arabic letter parameters E through I will be automatically optimized; the others will be set manually. As a result, some 20 calculations will be discussed in subsection 4.

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*The parameter E, not γ and δ, essentially determines the % yield $\underset{\sim}{5}$. However, if γ and δ are varied, E must follow in order to get % yield $\underset{\sim}{5}$/% yield $\underset{\sim}{10}$ right.

2. Generalized Least-Squares Adjustment

A. The Normal Equations

Let us suppose that we have obtained N measurements of a quantity R, perhaps the ratio of two products of interest. These may all involve separate experimental conditions, or may include replicative measurements. Let us further suppose that a suggested description of the problem leads to a theoretical expression for R which is a function of three unknown parameters (a, b, and c) and of the reaction temperature T. Thus we have three parameters and two sets of observables (R_i^{obs} and T_i). We might wish to minimize the sum of the squares of the differences between calculated and observed values of R. The criterion would then be

$$S(a,b,c) = \sum_{i=1}^{N} \left\{ R_i^{calc}(T_i, a, b, c) - R_i^{obs} \right\}^2 , \quad \text{a minimum} \qquad (2.2\text{-}1)$$

However, this formulation is reasonable only if errors in R_i^{obs} are expected to be constant, rather than proportional to R_i^{obs}. The latter will probably more often be the better approximation. Suppose, for example, that R is a product ratio (like our R1 and R2) which is obtained as a ratio of peak areas measured by vpc. If resolution is adequate, we should expect that the probable errors in the peak area measurements will be some small, but reasonably constant, fraction of the peak areas. If this is so, the probable errors in R will be proportional to R, and we should really seek to minimize the sum of the squares of the <u>relative</u> differences in observed and calculated

values of R:

$$S(a,b,c) = \sum_{i=1}^{N} \left\{ \frac{R_i^{calc}(T_i, a, b, c) - R_i^{obs}}{R_i^{obs}} \right\}^2 \quad , \text{ a minimum} \qquad (2.2\text{-}2)$$

Minimizing the function S(a, b, c) (S, for short) means finding values of a, b, and c which simultaneously satisfy eqs. 2.2-3.

$$\frac{\partial S}{\partial a} = 0 \; ; \qquad \frac{\partial S}{\partial b} = 0 \; ; \qquad \frac{\partial S}{\partial c} = 0 \; ; \qquad (2.2\text{-}3)$$

If we knew the analytic dependence of S on the parameters a, b, and c, finding these values would be trivial. Not in general having that information, we proceed to do the next best thing, which is to expand S in a Taylor series, truncated where required for mathematical tractability. Let us suppose that we have a set of estimates a^o, b^o, c^o of the desired parameters a, b, and c. Then expanding S to second order about the known point, we have

$$\begin{aligned} S(a,b,c) = {} & S(a^o,b^o,c^o) - \Delta a\, S_a - \Delta b\, S_b - \Delta c\, S_c \\ & + \tfrac{1}{2}(\Delta a)^2 S_{aa} + \tfrac{1}{2}(\Delta b)^2 S_{bb} + \tfrac{1}{2}(\Delta c)^2 S_{cc} \\ & + \Delta a \Delta b\, S_{ab} + \Delta a \Delta c\, S_{ac} + \Delta b \Delta c\, S_{bc} \quad , \end{aligned} \qquad (2.2\text{-}4)$$

where, for example,

$$\Delta a \equiv a^o - a \; ; \quad S_a \equiv \left(\frac{\partial S}{\partial a}\right)\Big|_{(a^o,b^o,c^o)} \; ; \quad S_{ab} \equiv \left(\frac{\partial^2 S}{\partial a \partial b}\right)\Big|_{(a^o,b^o,c^o)} \; .$$

All but the delta quantities in eq. 2. 2-4 are simply numbers evaluated at the point (a^o, b^o, c^o). Differentiating eq. 2. 2-4 with respect to a, b, and c, and recalling eq. 2. 2-3, we see that the unknown quantities Δa, Δb, Δc must be chosen to simultaneously satisfy eqs. 2. 2-5:

$$\left.\begin{aligned} \frac{\partial S}{\partial a} &= S_a - \Delta a\, S_{aa} - \Delta b\, S_{ab} - \Delta c\, S_{ac} = 0 \\ \frac{\partial S}{\partial b} &= S_b - \Delta a\, S_{ba} - \Delta b\, S_{bb} - \Delta c\, S_{bc} = 0 \\ \frac{\partial S}{\partial c} &= S_c - \Delta a\, S_{ca} - \Delta b\, S_{cb} - \Delta c\, S_{cc} = 0 \end{aligned}\right\} \qquad (2.\ 2\text{-}5)$$

Our immediate problem thus reduces to the solution of three simultaneous linear equations. This solution can be effected in several ways, one of which is discussed below. When the values of the delta equations have been found, they are combined with the estimates (a^o, b^o, c^o) to obtain new values of the parameter, viz.:

$$\begin{aligned} a &= a^o - \Delta a \\ b &= b^o - \Delta b \\ c &= c^o - \Delta c \end{aligned} \qquad (2.\ 2\text{-}6)$$

If the (a^o, b^o, c^o) are sufficiently good that negligible error is made at (a, b, c) in taking the Taylor series expansion of S about (a^o, b^o, c^o) only to second order, the (a, b, c) will be the least-squares estimates of the parameters. Generally, however, this will not be the case, and one must take the (a, b, c) as a new initial approximation (a^o, b^o, c^o). Of course, the iteration may diverge if the initial

approximation (a^o, b^o, c^o) is not good enough. Then one must select a new trial set (a^o, b^o, c^o) and try again.

Let us now examine how the first and second derivatives of S can be calculated. At a very preliminary and restricted stage of calculations of the type reported in this Section, the derivatives were obtained numerically. This was done by writing a control routine to feed the variations of the initial parameter set (with all combinations of zero, one, or two parameters incremented or decremented by predetermined amounts) to the main program which assembled S. Then the derivatives were calculated by finite differences. The minimum number of sets of calculations of S required to assemble the necessary derivatives is $2n^2 + 1$, where n is the number of parameters. Clearly, the computer time required for calculating the derivatives in this way increases more strongly with the number of parameters than one would like. In addition, the approximation of using finite differences can lead to severe problems of numerical stability. However, for situations involving exceedingly complicated expressions of a small number of parameters, numerical differentiation may be the method of choice.

In general, we can do better by evaluating the derivatives analytically. We begin by rewriting eq. 2.2-2 in the form

$$S = \sum_{i=1}^{N} \frac{(F_i^o)^2}{(R_i^{obs})^2} \qquad (2.2\text{-}7)$$

where $F_i^o \equiv R_i^{calc} - R_i^{obs}$. Differentiating eq. 2.2-7 with respect to the parameter a gives

$$S_a = 2 \sum_{i=1}^{N} \frac{F_i^{\,o} F_{a_i}}{(R_i^{\,obs})^2} \quad , \tag{2.2-8}$$

where

$$F_{a_i} = \left(\frac{\partial F_i^{\,o}}{\partial a} \right)\Big|_{(a^o, b^o, c^o)} = \left(\frac{\partial R_i^{\,calc}}{\partial a} \right)\Big|_{(a^o, b^o, c^o)} \quad . \tag{2.2-9}$$

Differentiation of eq. 2.2-8 with respect to a second parameter, say c, gives

$$S_{ac} = S_{ca} = 2 \sum_{i=1}^{N} \left\{ \frac{F_{a_i} F_{c_i} - F_i^{\,o} F_{ac_i}}{(R_i^{\,obs})^2} \right\} \quad . \tag{2.2-10}$$

Thus we see that to take advantage of the presumed accuracy of an expansion of S through second order, we require all of the first and second derivatives of $R_i^{\,calc}$ with respect to the parameters. For a case of 10 parameters (the number we shall employ in the least-squares treatment of the ratios R1 and R2 of subsection 2), this would amount to 10 first derivatives of R^{calc} plus 55 second derivatives (all those on or above the diagonal of a 10×10 matrix). However, we can generally make do with only the first derivatives of R^{calc}. The reason is that the second derivative terms (F_{ac_i} in eq. 2.2-10) are multiplied by $F_i^{\,o}$, which for a refined fit will sometimes be positive and sometimes negative. The result is a tendency to cancel when summed over the data points. We shall likely be left with a slower rate of convergence and perhaps a smaller radius of convergence, but in many cases this is a

small price to pay. The fit to the product ratios R1 and R2 described in this Section is one such case; because of implicit dependencies, the first derivatives of the product-ratio expressions are difficult enough to work out.

If we further define

$$L_i = (R_i^{obs})^2 \quad , \tag{2.2-11}$$

for reasons which will shortly be apparent, the system of equations (eqs. 2.2-5) becomes:

$$\begin{aligned}
\sum \frac{F_{a_i} F_{a_i}}{L_i} \Delta a + \sum \frac{F_{a_i} F_{b_i}}{L_i} \Delta b + \sum \frac{F_{a_i} F_{c_i}}{L_i} \Delta c &= \sum \frac{F_{a_i} F_i^o}{L_i} \\
\sum \frac{F_{b_i} F_{a_i}}{L_i} \Delta a + \sum \frac{F_{b_i} F_{b_i}}{L_i} \Delta b + \sum \frac{F_{b_i} F_{c_i}}{L_i} \Delta c &= \sum \frac{F_{b_i} F_i^o}{L_i} \\
\sum \frac{F_{c_i} F_{a_i}}{L_i} \Delta a + \sum \frac{F_{c_i} F_{b_i}}{L_i} \Delta b + \sum \frac{F_{c_i} F_{c_i}}{L_i} \Delta c &= \sum \frac{F_{c_i} F_i^o}{L_i}
\end{aligned} \tag{2.2-12}$$

where the summations go from 1 to N as usual.

These are the so-called normal equations. They are rigorously derived in many places, notably in Deming's 'Statistical Adjustment of Data' (26a). Deming's derivation is recapitulated, with examples of chemical interest, by Wentworth in the Journal of Chemical Education (26b). That derivation begins with the assumption that the errors in the observables (here, the product ratios R_i^{obs} and the reaction tem-

perature T_i) are random and belong to a Gaussian distribution. In the minimization procedure, which is set up in quite different form from the approach given here, one performs a set of constrained variations. As is commonly done, Lagrange multipliers are invoked to handle the constraints. One then works out what the Lagrange multipliers must be and comes out with eqs. 2.2-12, where the factors L_i are found to be given by a sum containing a term of the form $\left(F_{x_i}\right)^2/W_{x_i}$ for each of the observables. F_{x_i} is the derivative of F_i^o with respect to the observable x and W_{x_i} is the weight of observable x for the i-th observation. Specifically,

$$W_{x_i} = \left(\frac{\sigma_o}{\sigma_{x_i}}\right)^2 , \qquad (2.2\text{-}13)$$

where σ_{x_i} is the standard error in the i-th measurement of the observable x and σ_o is an arbitrary constant* of convenient magnitude.

For our product-ratio example, then, L_i will have two terms:

$$L_i = \left(\frac{\partial F_i^o}{\partial R^{obs}}\right)^2 \left(\frac{\sigma_{R_i}^{obs}}{\sigma_o}\right)^2 + \left(\frac{\partial F_i^o}{\partial T}\right)^2 \left(\frac{\sigma_{T_i}}{\sigma_o}\right)^2 \qquad (2.2\text{-}14)$$

$$= \left(\frac{\sigma_{R_i}^{obs}}{\sigma_o}\right)^2 + \left(\frac{\partial R_i^{calc}}{\partial T}\right)^2 \left(\frac{\sigma_{T_i}}{\sigma_o}\right)^2$$

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*Note that σ_o will affect each of the terms in eqs. 2.2-12 equally. Therefore, the values of the delta quantities do not depend on the choice of σ_o.

If the errors in R_i^{obs} are assumed to be proportional to R_i^{obs} where the proportionality factor is 0.05 (i.e., $\sigma_{R_i^{obs}} = 0.05\, R_i^{obs}$) and σ_o is taken to be 0.05, we have that

$$L_i = R_i^{obs\ 2} + \left(\frac{\partial R_i^{calc}}{\partial T}\right)^2 \left(\frac{\sigma_{T_i}}{0.05}\right)^2 . \qquad (2.2\text{-}15)$$

Comparison with eq. 2.2-11 shows that we were only approximately correct in originally defining S in terms of eq. 2.2-2: we accounted for errors in R_i^{obs} arising from our hypothetical vpc area measurements, but failed to account for the possibility that deviations between observed and predicted values of R_i might also arise from inaccuracy in the measurement of the reaction temperatures T_i. The second term in eq. 2.2-14 tells us, very reasonably, that the importance of errors in the latter is to be judged according to how sensitive R_i is to the reaction temperature and how uncertain is our measurement of that temperature. For many cases, however, including that of the real product ratios R1 and R2 of this Section, the dominant uncertainty is usually that in the measurement of the product ratio, rather than that in the measurement of the reaction temperature (or other observables, such as the hydrogen-donor concentration).

The normal equations are quite general, and we see that a simple recipe exists for setting them up. First one defines an expression F_i^o involving the observables and the unknown parameters which would be zero for each measurement i if the true values of the parameters and

of the observables could be employed. In the present example, $R_i^{calc} - R_i^{obs} = 0$ under such conditions. The factors L_i are then evaluated in terms of the derivatives of F_i^o with respect to the observables and assumed or statistically inferred standard errors in the measurements of the observables. Then F_i^o and its derivatives with respect to each of the unknown parameters are evaluated for the current approximations to those parameters. The normal equations then compiled as in eqs. 2.2-12. Finally, the set of simultaneous linear equations is solved (see below) for the difference quantities and the estimates of the parameters are updated. If necessary, the process is repeated.

We have not actually derived the normal equations here, although the present treatment would have constituted a derivation if we had started out with the correct form of S, namely

$$S = \sum_{i=1}^{N} \frac{(F_i^o)^2}{L_i} \quad . \qquad (2.2\text{-}16)$$

However, rigorously obtaining the definition of L_i is not a trivial matter for one unschooled in probability theory. We have preferred simply to invoke the definition with a few comments on its reasonability.

Alternatively, Deming's derivation could have been recounted. However, its reliance on faintly mystical Lagrange multipliers might well serve to elicit a feeling of beauty on the part of the mathematical purist, but of confusion on the part of the chemist (the latter, at least, was its effect on this chemist). Better, we have therefore thought, to

employ the present approach, where the criterion for minimization--the simultaneous vanishing of all the first derivatives of S--and the use of the familiar Taylor series expansion should provide a solid physical basis for understanding how the normal equations come to take their peculiar form.

B. The Reciprocal Solution

We still have several matters to transact to complete the description of least-squares adjustment. For example, we have yet to consider how the normal equations may be solved for the difference quantities. Especially convenient, if a digital computer is available, is the so-called reciprocal solution (26). This method of solution involves the recognition that the left-hand sides of eqs. 2.2-12 can jointly be expressed as the product of a square matrix $\underset{\sim}{\underset{\sim}{S2}}$ (for second derivatives of S--3 × 3 in the example considered here) with a column vector $\underset{\sim}{D}$ (for delta quantities; e.g., $\underset{\sim}{D}_a = \Delta a$). The result is a column vector $\underset{\sim}{\underset{\sim}{S1}}$ (for first derivatives of S with respect to the parameters):

$$\underset{\sim}{\underset{\sim}{S2}} \times \underset{\sim}{D} = \underset{\sim}{\underset{\sim}{S1}} \qquad (2.2\text{-}16)$$

If we then find the inverse of $\underset{\sim}{\underset{\sim}{S2}}$ ($\equiv \underset{\sim}{\underset{\sim}{S2}}^{-1}$) and left-multiply it into eq. 2.2-16, we obtain

$$(\underset{\sim}{\underset{\sim}{S2}}^{-1} \times \underset{\sim}{\underset{\sim}{S2}}) \times \underset{\sim}{D} = \underset{\sim}{\underset{\sim}{S2}}^{-1} \times \underset{\sim}{\underset{\sim}{S1}} = \underset{\sim}{D} \quad ,$$

and the difference quantities have been found.

The importance of this method of solution derives from the fact